This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

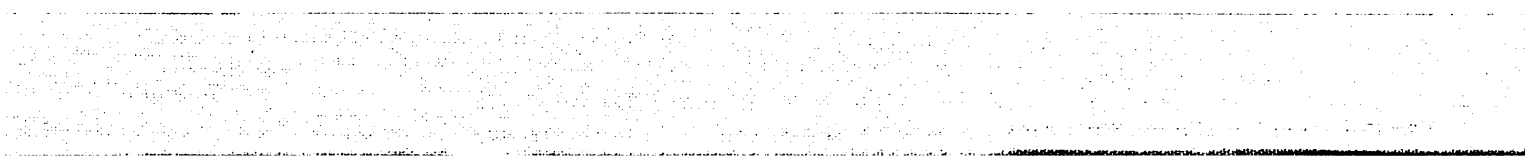
+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`

NYPL RESEARCH LIBRARIES
3 3433 06911107 2



THE ELEMENTS

OF

ELECTRO-CHEMISTRY

TREATED EXPERIMENTALLY

SCIENCE DEPT.
Luepk
3-P1

(I 4)

THE ELEMENTS

OF

ELECTRO-CHEMISTRY

TREATED EXPERIMENTALLY

BY

DR. ROBERT LÜPKE

Headmaster of the Municipal Dorothea Realgymnasium, and Lecturer in the Imperial School of Posts and Telegraphs, Berlin

TRANSLATED FROM THE SECOND, REVISED AND ENLARGED, EDITION BY

M. M. PATTISON MUIR, M.A.

Fellow and Lecturer of Gonville and Caius College, Cambridge

With Fifty-four Figures in the Text

LONDON

H. GREVEL & CO.

33, KING STREET, COVENT GARDEN, W.C.

1897

Printed by Hazell, Watson, & Viney, Ld., London and Aylesbury.

PREFACE

TO THE FIRST EDITION.

THE researches in physical chemistry which have been prosecuted with great eagerness during the last two decades have led to results whereby many of the problems of exact science which had remained unsolved have been answered. For instance, a deeper insight has been obtained into the nature of solutions, by the work of van't Hoff, who has shown that the law of Avogadro, which had been applied only to gases, holds good also for substances in solution. This result has been of especial importance to electro-chemistry, although at first sight it appears to have no connection with that subject. It may be affirmed to-day that the conduction of the galvanic current in electrolytes, as well as the origin of the current in galvanic cells, matters which had been discussed for a century, have been explained.

The science of electro-chemistry is set forth in detail in researches published in various journals, and in the text-books

of physical chemistry of Ostwald and Nernst. Nevertheless I have undertaken to write this short book, because I thought the time to be opportune for bringing together the new results in a condensed form, and for giving a short survey to those who are not in a position to make an exhaustive study of the voluminous literature of the subject for themselves. In order to make the theories, which are difficult in themselves, more easily intelligible to the reader, who is assumed not to have more than a knowledge of the fundamental conceptions of physics and chemistry, the various laws have been deduced directly from the experimental results. Mathematical discussions have been introduced for the purpose of more complete confirmation only in a very few cases.

The experiments which form an essential part of this book are carried out with the simplest possible apparatus.* They are arranged to make the process that is under consideration clearly intelligible, and also to ensure the attainment of the final result in as short a time as possible. For this reason they may be made especially useful for teaching, and also for becoming practically acquainted with the physical and chemical properties of various substances. It is true that very accurate results are not to be expected in the experiments wherein measurements are made; for more delicate instruments, such as are to be found only in scientific laboratories, are required in order to obtain accurate numerical results; but, at the same time,

* Much of the apparatus may be prepared by the student himself. The rest can be obtained from Glass-blower Max Stuhl (Berlin, N., Philippstrasse 22).

ch instruments are not generally suitable for the purposes of demonstration.

Although the main purpose of the book is to set forth ıe purely scientific aspects of electro-chemistry, the ›ractical sides of the subject have not been left altogether ınnoticed. Technical electro-chemical processes, and especially the processes of electro-metallurgy, which are so important at present, are referred to in their proper places.

ROBERT LÜPKE.

BERLIN, *May 1st*, 1895.

PREFACE

TO THE SECOND EDITION.

A SECOND Edition of my "Elements of Electro-chemistry, treated experimentally," was called for a few months after the appearance of the book. This showed me that there was want of a book setting forth succinctly the most important parts of electro-chemistry, and that the method of the book, which deduces the laws and elucidates the theories from the basis of experiments, had met with approval. Several works on electro-chemistry, it is true, have appeared in the course of a year, such as those of Ostwald, Jahn, Le Blanc, and Ahrens, to which my "Elements" are much inferior, looked at from the scientific standpoint. Nevertheless I hope that those readers who wish to make a preliminary survey of electro-chemistry before they enter on the study of the more detailed works will receive the second edition of my book with favour.

So far as time allowed, I have enlarged the first edition here and there, and made it more complete. The chapter

... with the energetics of the galvanic ele... ...
... ...ifferent, and more attention has been give... ...
... ...ld of electrochemistry, as regards the p... ...
... ...ocesses that have received practical applica... ...

ROBERT LÜP...

April 10th, 1896.

TRANSLATOR'S NOTE.

... small changes have been made in the English ... with the sanction of the Author.

... small additions made here and there by the Translator are included in square brackets.

March, 1897.

TABLE OF CONTENTS.

PAGES

TRODUCTION 1–2

PART I.

RECENT THEORIES OF ELECTROLYSIS.

HAPTER I. THE PHENOMENA OF ELECTROLYSIS 4–31

(i.) *The Electrolysis of fused compounds* 4–9

Preparation of magnesium from magnesium-potassium chloride 4

„ „ aluminium from aluminium-potassium chloride . 6

Calcium carbide and silicon carbide 8

Electrolysis of fused lead chloride 8

„ „ caustic potash 9

(ii.) *The Electrolysis of compounds in solution* 9–19

Electrolysis of zinc chloride 9

„ „ stannous chloride 10

„ „ hydrochloric acid 11

„ „ sodium chloride, and electrical bleaching . . 12

Electrical preparation of potassium chlorate 13

Electrolysis of copper sulphate between copper electrodes . 14

Principle of electro-plating and etching 15–16

Electrolysis of copper sulphate between a copper kathode and a platinum anode 16

Electrolysis of dilute sulphuric acid between a platinum kathode and a copper anode 17

Electrolysis of alkali salts of oxyacids 18

Reagents for discriminating the galvanic poles 19

The conceptions of Berzelius and Daniell regarding salts . 20

Hittorf's conception of an electrolyte 22

Chapter V. The Dissociation Theory of Arrhenius
Work done by the current during electrolysis 57–73
Coefficient of dissociation 57–58
Conductivity of pure water 59
Capability of dissociation of the solvent 60
Heat of ionisation according to Ostwald 60–62
Theories of Grotthus and Clausius regarding current-conduction 63–66
Energy-contents of the ions 67–68
Explanation of chemical change by the dissociation theory; activity-coefficients 68
Thermoneutrality of solutions 69–70
Proof of the [illegible] of free ions 70
71–73

PART II.

THE THEORY OF SOLUTIONS OF VAN'T HOFF.

PAGES

CHAPTER I. OSMOTIC PRESSURE 75–91

Diffusion of dissolved substances and the conception of osmotic pressure 75–76

Semipermeable membranes 77

Plasmolysis and the law of H. de Vries 77

Traube's proof of osmotic pressure 78

Pfeffer's measurement of osmotic pressure 79–83

„ laws of osmotic pressure 84

Horstmann's gaseous equation 84–87

The law of van't Hoff 88

Osmotic work done by solutions 89–90

Magnitudes of osmotic pressures 91

CHAPTER II. THE VAPOUR-PRESSURES OF SOLUTIONS . . 92–99

Vapour-pressure of a solution 92

Raoult's laws of vapour-pressures of solutions 93

„ measurement of vapour-pressures of solutions . 94–97

Relation between osmotic pressure and vapour-pressure of a solution (Ostwald) 97–99

CHAPTER III. BOILING POINTS AND FREEZING POINTS OF SOLUTIONS 100–110

Rise of boiling, and lowering of freezing, point of a solution 100–101

Beckmann's measurement of boiling point 101–104

Raoult's laws of increment of boiling point 104

Determination of molecular weights by the boiling point method 105–106

Raoult's laws of lowering of freezing point 107–108

Determination of molecular weights by the freezing point method 109–110

CHAPTER IV. SUMMARY 111–116

Relations between osmotic pressure and decrease of vapour-pressure, increase of boiling point, and lowering of freezing point (van't Hoff) 111–113

Calculation of molecular lowering of freezing point by van't Hoff 113–116

CHAPTER V. AQUEOUS SOLUTIONS OF ELECTROLYTES . . 117–121

Carrying over of the law of van't Hoff to solutions of electrolytes 117–118

Explanation of the factor i by Arrhenius, and confirmation of the dissociation theory 119–121

PAGES

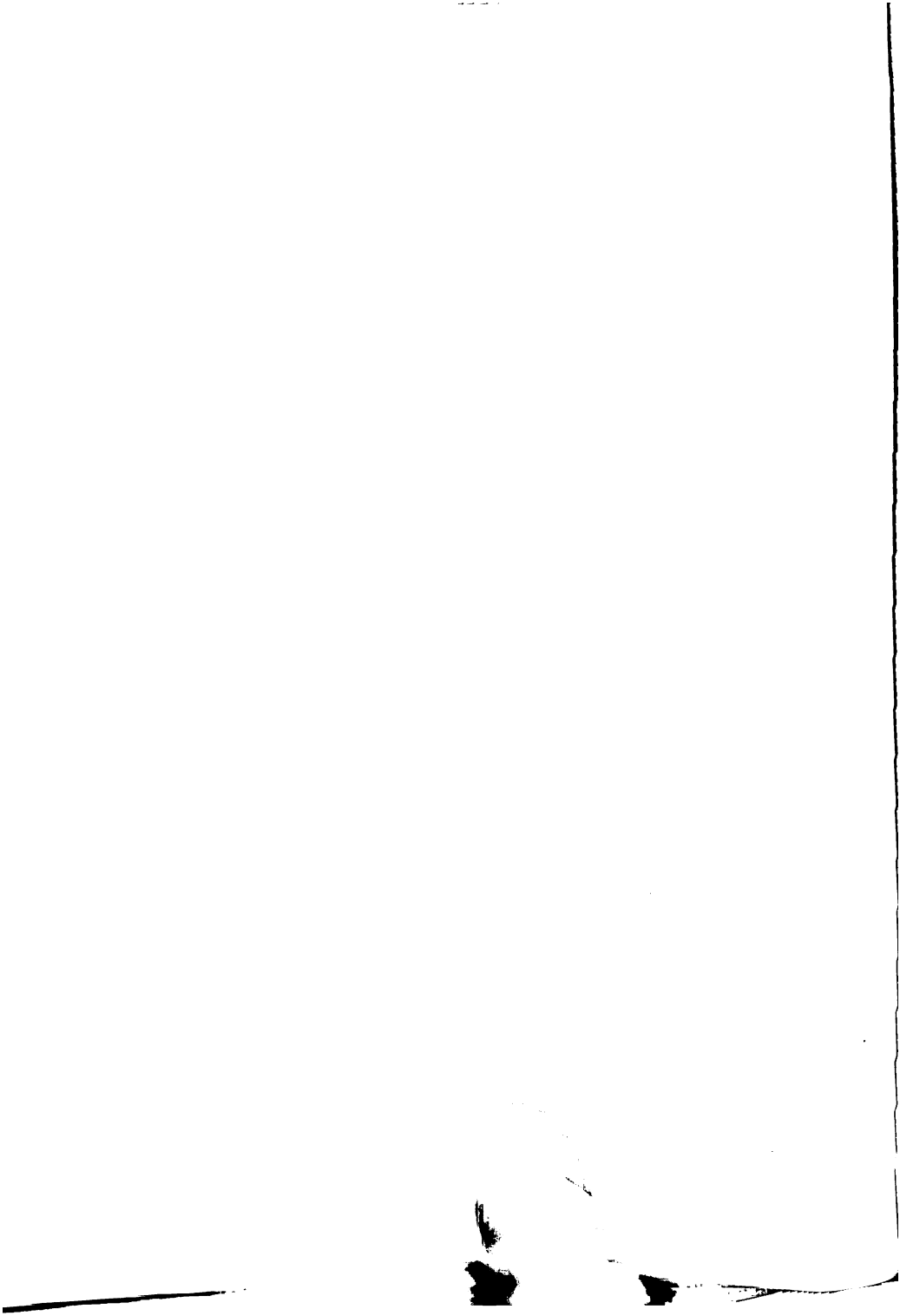
'TER VI. INTENSITY OF FIXATION, AND POLARISATION . 171–185
lectrolysis with soluble and insoluble anodes . . . 171–172
'olarisation-currents 173–175
.e Blanc's intensity of fixation of the ions 176
'elation of E.M.F. of Daniell cells to intensities of fixation . 177
Intensities of fixation of potassium and hydrogen ions . . 178
)ecomposition-tensions of electrolytes 179
'lectrolytic separation of the metals 181–183
'lectrical purification of copper 183
'lectrical preparation of copper by the processes of Siemens and Höpfner 184

PTER VII. IRREVERSIBLE CELLS 186–196
Polarisation of inconstant cells 186
Constant irreversible cells 188
Depolarisation in Bunsen cells 189
Actions of different depolarising agents 192
Leclanché cells 193

\PTER VIII. ACCUMULATORS 197–206
The action of the electrodes in leaden accumulators . . . 197
Planté's method of preparing accumulators 200
Charging accumulators by means of copper elements . . . 201
The zero-effect of accumulators 204
Self-discharging accumulators 205

APTER IX. THE ENERGETICS OF GALVANIC ELEMENTS . 207–218
Total heat in the element and in the connecting wire . . . 207
Chemical work done by the current 211
Transformation of chemical energy into electrical energy . . 212
Chemical changes in leaden accumulators 216
Peltier's effect and its relation to the temperature-coefficients of galvanic elements 217

NDEX 219



THE ELEMENTS OF

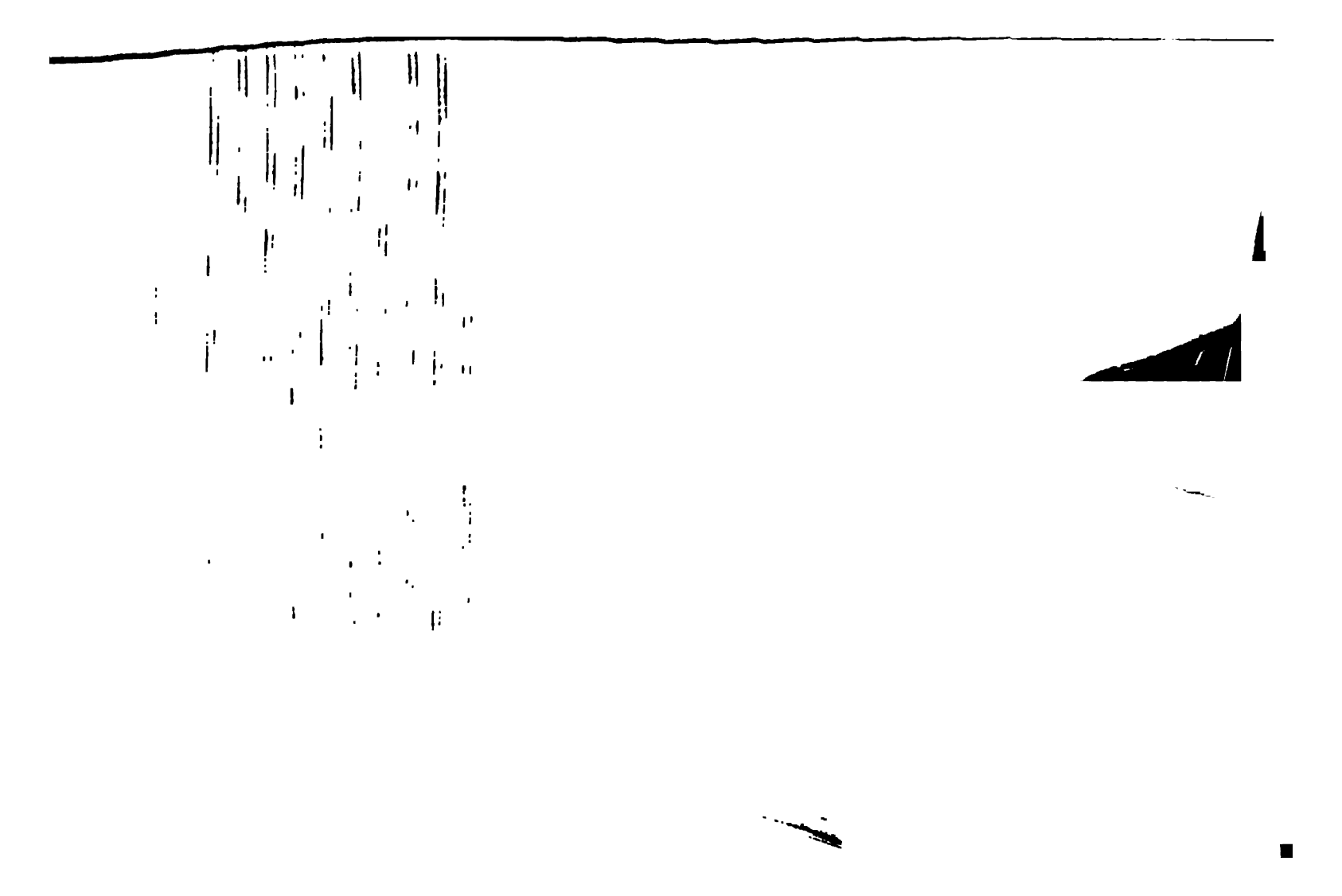
ELECTRO-CHEMISTRY.

INTRODUCTION.

HUNDRED years have passed since the discovery of the ltaic battery, that simple apparatus which has been the arting-point of all those instruments wherein galvanic rrents are obtained by combining conductors of the first id second class. But although voltaic batteries have been ed for so long a time it was not until quite recently that ie theory of their action was made clear; for the theories iat had been advanced, the contact theory and the chemical ieory, did not suffice to give a satisfactory explanation of ie production of the galvanic current.

Nernst was the first to give a clear representation of the iechanism of the formation of the current by his *osmotic heory*, put forward by him at Göttingen in 1889.

The theory of Nernst is based on a broad and firm founda- ion. It assumes certain other theories, also of recent date, *hich are concerned with* the most important parts of the oungest branch *of scientific* chemistry, to wit physical hemistry. *It takes especial* account of Helmholtz's theory



PART I.

RECENT THEORIES OF ELECTROLYSIS.

E term *electrolysis* refers to the chemical changes which ır when an ' electric current passes through a *conductor the second class.* Such a conductor, which is always a mical compound either in solution or fused, is called an *trolyte* (λύω = loose). *Conductors of the first class*, which, he form of wires or plates, lead the current into, or away m, electrolytic cells, are called *electrodes* (ὁδόω = lead , one being called the *anode* and the other the *kathode* ἄνοδος = the way up; ἡ κάθοδος = the way down). The ɔ latter terms are derived from the supposition that the th's magnetism is caused by electrical currents which flow ɔund the earth parallel to the degrees of latitude, in the ection from east to west, that is from the rising to the ting sun. Because of the difference of potential that is used on the electrodes by the electrolysing current, the o essentially distinct particles of the electrolyte move in fferent directions, one towards the anode and the other wards the kathode. These minute particles, which travel the directions just indicated, are called *ions* (ἰών, *gen.* ντος, = going); *anions* being those which go to the anode, nd *kations* those which go to the kathode. The chemical hanges brought about by the ions at the electrodes are called lectrolysis. As we shall see in the first chapter, the results f these changes may differ very much, according to the onditions that prevail.

CHAPTER I.

THE PHENOMENA OF ELECTROLYSIS

The best cases of electrolysis are shown in the simplest way when fused binary compounds are used, because in these the products separate directly on the electrodes.

Lassaigne and Stanislas Meunier (*Anorganische Chemie*, 1871, p. 517) has described a lecture-experiment, with a clay tobacco-pipe, for demonstrating the electrolysis of magnesium chloride, which has been frequently performed by Bunsen. Potassium-magnesium chloride, a salt that can be fused easily in a platinum dish, is used as the electrolyte. The salt is obtained in the fused condition by evaporating to dryness, on the water-bath in a platinum basin, a solution of 30 grams crystallised magnesium chloride and 7·5 grams potassium chloride, with addition of a little ammonium chloride, and then rapidly heating the solid residue by a blowpipe flame. The fused mass is poured into the bowl of an unglazed pipe (*p* in fig. 1), which has been previously strongly heated, and which is supported in a clay triangle. The current from ten accumulators * arranged *in series*

* Accumulators made by W. A. Boese & Co. Berlin S.O. Köpenickerstrasse 54, very suitable for laboratory purposes. The plates are entirely of a mass of active material enclosed in a complex network of ebonite rods, 12 centims wide, 15 centims high, 12 centims thick, and weighing 2·5 kilos. When discharged completely they are superchloride of lead. A discharged accumulator can be charged with a current of 4 ampères in about 8 hours, and will then give a current of 4 ampères for about 8 hours. The real size of the accumulators is 20 per cent.

is, one behind the other) is then sent through the fused
knitting-needle which is passed through the stem of
pe serving as kathode (*k* in fig. 1), and a rod of carbon
dips into the bowl being used as anode (*a* in fig. 1).
ugh the heat produced by the current soon liquefies the
et it is better to place a small flame beneath the bowl of
be.

orine is easily detected by bringing a piece of moistened
paper near
ode [the paper
ached by the
e]. But the
part of the
sium burns on
rface of the
salt, which
ly fumes and
, and when
paratus is al-
to cool the
um is dis-
d through
s in such fine
that its sil-
re cannot be

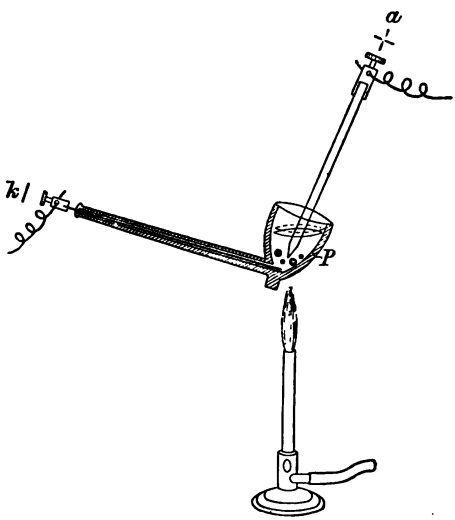


Fig. 1.

. Both drawbacks are easily obviated by covering
d electrolyte with a thick layer of finely powdered
arcoal, immediately after closing the circuit. The
g is thus avoided, and after allowing the current to
barely twenty minutes a great many lustrous pellets
esium, from 1 to 2, and sometimes even 5, mm.
can be obtained when the cold mass is broken
e pellets should be isolated by rubbing the mass

in a mortar along with about; they may be bu
the production of bright light lasting for fifteen
seconds, by wrapping them round in a little loop o
wire-gauze and igniting them in a flame. The pell
be melted to a regulus by putting as much powdered
as will lie on the tip of a spatula into the bowl of th
at the close of the electrolysis, and heating the bowl s
for ten minutes.

Aluminium also can be obtained in the form of l
pellets by a process similar to that described; and th
particles may be united into one piece by throwing
into fusing common salt. The reaction characteris
aluminium is obtained by dissolving the pellets in h
chloric acid, adding an excess of pure potash solution
precipitating aluminium hydroxide by addition of ammo
chloride.

There is however some difficulty in preparing anhyd
aluminium—potassium chloride, which was the salt usec
Bunsen in 1854, and is the only salt suitable for emp
ment as an electrolyte in this experiment. Dry alumin
chloride is prepared by passing a stream of dry hydroch
acid gas over aluminium that is heated strongly. The e
way of the tube containing a current of hydrochloric acid gas,
still contains for four to six hours, and which c
liquid, to allow concentrated sulphuric acid t
hydrochloric acid. Figure 2 sho
of the apparatus; the hydrochloric
and the sulphuric acid drops f
II. The hydrochloric acid g
concentrated sulphuric acid in
into a tubulated vessel
capacity, which contains fr
cut into small pieces, a

l by a large Bunsen lamp. After some time aluminium
le is deposited in the wide neck of the receiver (*h*) as
te sublimate, and when the action has proceeded for
r three hours the deposit of chloride is removed by
of a knife. As aluminium chloride is very hygro-
the salt must be transformed into the more stable
chloride as soon as it is removed from the neck of

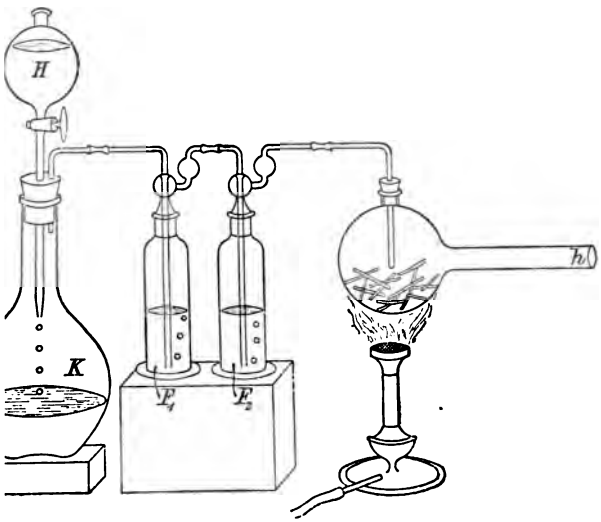


Fig. 2.

ver. For this purpose all that is required is to melt
s of potassium chloride in a platinum crucible, and
ne part of aluminium chloride, in successive portions,
:onstantly, and then to pour out the melted mass on
:e of porcelain. The double salt must be kept in
stoppered jar.

principle of the experiment wherein the double
m-potassium chloride is electrolysed is the same as

that of the technical preparation of aluminium by the electrolytic process. The main difference between the two processes lies in the fact that in the manufacturing operations pure aluminium oxide, prepared from the mineral *bauxite*, is used as the electrolyte; the oxide of aluminium is thrown into fusing *cryolite*, in a Héroult oven, and a current of great intensity is passed through the mass.

Special emphasis must be laid on the fact that in those preparations of very infusible metals which have been performed recently by electrical methods, for instance the preparation of chromium and tungsten (and also of the carbides of calcium and silicon *), the electric current does not cause electrolysis, but that it acts only as a source of heat which is sufficiently intense to cause the reduction of the oxides of the elements used, in the presence of carbon.

Fused lead chloride is much more easily decomposed by the current than compounds of magnesium or aluminium, and, for this reason, the lead salt is more suitable for demonstration purposes. As lead chloride is somewhat volatile when heated, the salt ought to be melted, in a porcelain crucible, in a draught place, before it is put into the bowl of the pipe. A sufficiently large regulus of lead is obtained by passing

...five accumulators for about ten minutes.

...ured out on to a piece of porcelain,

...is exposed by rubbing with a file.

...s the most suitable base to electrolyse

...ercury is poured into a

...f the dish; a few sticks

...nd these are melted by

...ion of acetylene gas, which is

..., while silicon carbide is used,

...g because of its very great

ing the vessel by a small flame; the current from about accumulators is then sent through the melted potash, the n being used as the kathode, while a piece of platinum sunk into the electrolyte serves as the anode. The mposition proceeds in accordance with the scheme $)H = 2K + H_2O + O$. The potassium alloys with the ury, and the oxygen passes off from the surface of the ium foil. After about half an hour the liquid amalgam ured into a test-tube, where it is allowed to solidify. It is o prove the presence of potassium by placing the alloy small flask arranged for preparing a dding diluted hydrochloric acid, and ing the hydrogen that comes off; about litre of hydrogen may be obtained hort time.

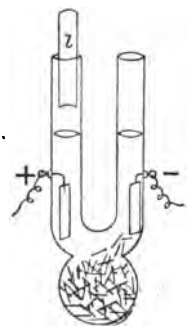


Fig. 3.

lead and chlorine can be separated used lead chloride, so the two con- :s of zinc chloride, zinc and chlorine, obtained by the decomposing action ectric current on a *concentrated aqueous* of the salt zinc chloride. The electro- conducted in a bulbed U-tube, containing two n plates [connected with platinum wires which pass the U-tube], the limbs of the tube being about gth and diameter of ordinary test-tubes. (*See* If ten accumulators are employed the bulb of l be filled with elegant, branching crystals of t twenty minutes; and if a piece of litmus n the limb of the tube which contains the er will be bleached, very quickly, by the coming off.

is made of the metal of the salt which is anode will be gradually dissolved by the

igth, new branches appear, in a regular way, between that have been formed already. Meanwhile the process nching repeats itself on the branches which were first ed. One of these branches becomes larger than the , and, as the increase of the upward-curving end of it es slower, this branch stretches in the direction of the nd the process begins anew. In this way the formation es downwards in a regular manner, until, when the is nearly reached, the weight of the branches causes m to snap and the whole falls down. Other filaments d there fall in the same way. Meanwhile new stems ned, and these fill the upper third of the cylinder with strous ramifications.

e are not many electrolytic solutions from which both n be separated on the electrodes by a process of rsis. The solution of stannous chloride we have been ing is an example of such an electrolyte. Hydro- acid also belongs to this category; the volumetric sis of this compound is well known to be important olishing the fundamental chemical conception of ncy. This electrolysis is carried out, by Hofmann's in a U-tube, which is attached to an upright tube, rnished with a couple of glass stopcocks, and contains rodes of carbon (*compare* fig. 14, p. 33). It is however to obtain exactly equal volumes of gas in the two the U-tube; this is due partly to the solubility of and partly to the disengagement of oxygen from the d the difficulty increases the more dilute the electro- id is made. After many trials, a satisfactory result ned by electrolysing, in a Hofmann's apparatus with ectrodes cut from pure gas-coke and provided with crews which were soldered on, a mixture of 10 c.c. ochloric acid of specific gravity 1·125 and 150 c.c.

ing is easily understood from
four-sided vessel of a Bose
and note p. 4) is used as a cell.

: longitudinal grooves are cut in the thin side-walls of
:ssel; a clay diaphragm is placed in the middle groove,
plate cut from retort carbon, and provided with a
g screw, in each of the other grooves. A piece of
'ed cotton is spread, by means of four little wooden
)n that carbon plate which is to be used as the anode.
lectrolytic liquid, which is poured into the cell, is made
olving 50 grams of common salt, 5 grams of magnesium
e, and a few drops of hydrochloric acid, in a litre of
The cell is covered with a glass vessel, and the poles
ttery of five accumulators are placed on the electrodes;
ıort time so much of the red cotton as is immersed
liquid is completely bleached.

'ate of potassium is made in certain factories by the
ysis of a solution of potassium chloride, the basic lye
s formed around the kathode being transported from
time to the anode, where, at the higher temperature,
rine reacts in accordance with the equation

$$6KOH + 6Cl = KClO_3 + 5KCl + 3H_2O.$$

of the electrolytes that have been referred to are
ompounds, and in the majority of the cases mentioned
constituents of the electrolyte separate directly at the
:s. *Such a separation in two directions generally occurs*
equence of electrolysis, however complicated the molecule
:ctrolyte may be. The hydrogen, or the metal, or a
which represents the hydrogen, is always carried
:he kathode, by the primary reaction, and the rest of
:ule travels towards the anode. Then, either the ions
'ee on the electrodes, or secondary reactions occur
)etween the ions and the substances of which the
: are made, or between the ions and the electrolyte
ıter. The occurrence of these secondary reactions

current is then reversed; after three minutes the beam attains equilibrium, and after another three minutes it es in the opposite direction.

e experiment of electrolysing a solution of copper ate between copper electrodes illustrates the principle of oplating, and also the principles of the electrical purifica-

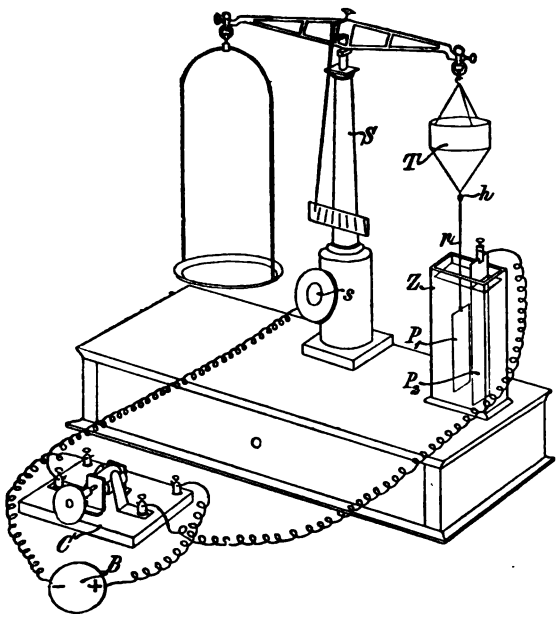
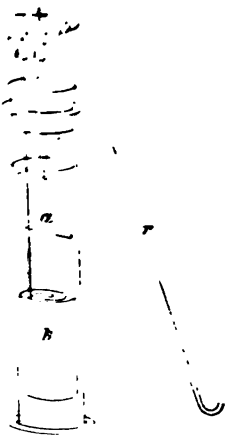


Fig. 5.

ude copper and the electrical separation of copper es of copper ore. (For more details see Part III., I.) The experiment also elucidates the mechanical galvanic etching of iron or copper vessels. The covered with a non-conducting etching varnish, en arranged as the anodes in acidified copper hs, after the pattern to be etched has been cut

through the covering of varnish. The deeply etched parts of the vessels can then be filled with other metals (silver, gold, etc.) by placing the vessels, as they are taken from the copper baths, as kathodes in baths of the metals to be deposited; an imitation of Oriental inlaid metal-work is thus produced.

The kind of etching that has been described is easily carried out on a small scale. A plate of polished copper is covered with melted wax, by the use of a pencil; a pattern is then cut through the wax by a knitting-needle, and the plate is exposed for about twenty minutes as the anode [in an acidified bath of a copper salt] to the action of a current from four cells. When the wax is then removed by turpentine, the pattern is seen eaten into the plate.



If the copper anode in an acidified copper bath is replaced by a plate of platinum, oxygen is disengaged on the platinum, in accordance with the equation

$$SO_4 + H_2O = H_2SO_4 + O;$$

al affinity of the platinum does not cause the ulphate under these experimental conditions.

he proc uitable for preparing small

xygen, ratus of Landolt, represented

ing ve athode, *k*, is a spirally rolled

ium, f platinum which is soldered

ire to it is covered with an isolating

ve cle is marked *a* in the figure,

ve the gas

Figure 7 represents an apparatus used for demonstrating that hydrogen is set free on the platinum kathode, *k*, when dilute solution of sulphuric acid is electrolysed, and that the ion SO_4 causes solution of copper from the copper anode, although copper does not otherwise dissolve in diluted sulphuric acid at the ordinary temperature. When a current from five accumulators has been passing for about ten

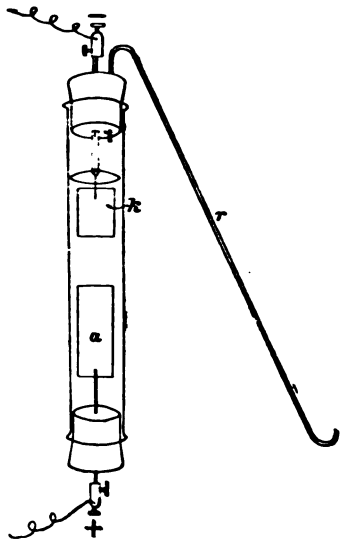


Fig. 7.

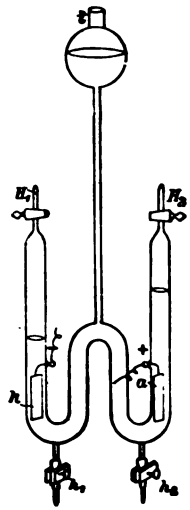


Fig. 8.

minutes, the liquid around the electrode *a* becomes distinctly blue, and pure hydrogen escapes by the tube *r*.

All acid salts are decomposed by electrolysis, primarily, into hydrogen or metal, and acid radicle.

The alkali metals seem, at the first glance, to form exceptions to this rule. If a cold concentrated solution of copper sulphate is electrolysed, in the apparatus represented in figure 8, between the platinum electrodes *k* and *a*, a current from ten accumulators being employed,

in alcoholic solution of phenolphthalein have been added. ien the circuit is closed the liquid round one of the :trodes becomes coloured rose-red: that electrode is in inection with the negative pole of the battery which is ng examined; for free alkali is formed at this electrode, l reacting with the phenolphthalein forms the red alkali t of that [slightly acidic] compound. If the cylinder is iken the red colour disappears, for the acid produced at : anode decomposes the salt and sets free phenolphthalein.* The use of "*pole-reagent paper*" is based on these reactions. iat reagent is blotting-paper soaked in potassium sulphate lution mixed with a very little solution of phenolphthalein; must be moistened before use. The reaction is more licate if the paper is impregnated with starch paste (2 : 100) which has been added one part of potassium iodide and a ry little phenolphthalein, then dried in air free from dust, id kept in a stoppered glass bottle. When the poles are id on this paper the negative pole is recognised, as before, y the production of a red colour, and a very dark blue olour is produced on the paper under the positive pole be- ause of the formation of "iodide of starch" by the iodine et free by the current. This paper enables an operator to ecognise the sign of one of the two poles of a battery when he other is led to earth, as is often the case in telegraph ffices; it is only necessary to lay the moistened paper on conductor connected with the earth, and to touch it with he doubtful pole. The action of this reagent may be made lear to a larger audience by passing a current through the mixed solutions already mentioned, but diluted ten times,

* According to Ostwald (see *Foundations of Analytical Chemistry*, p. 118), the alkali salts of phenolphthalein are ionised in dilute solutions, and the red colour is caused by the free ions; when an acid is added non-ionised phenolphthalein is formed, and this is colourless.—[TR.]

[illegible] the galvanometer: [illegible] that this is

Daniell gave an explanation of the electrolysis of salts ich was free from objections. He said that the current :omposes potassium sulphate, as it decomposes every other t, between platinum electrodes, into metal and acidic licle: but in the case of potassium sulphate both these ducts of decomposition enter into secondary reactions h the water; the potassium reacts at the kathode in ordance with the equation

$$2K + 2H_2O = 2KOH + H_2,$$

d the SO_4 reacts at the anode in this way—

$$SO_4 + H_2O = H_2SO_4 + O.$$

ie gases that are given off are, therefore, secondary pro- cts; and it is thus explained why the volumes of both ses are equal to the volumes of the same gases obtained in e voltameter, and are also equivalent to the quantities of id and base observed at the electrodes. It is possible to parate potassium directly from solutions of its salts, because mercury is used as the kathode the potassium forms an nalgam with that metal, and the action of water on this nalgam becomes apparent, by the evolution of little bubbles hydrogen, only some time after the closing of the circuit.

In accordance with the results of electrolyses, Daniell said at *every salt is a compound of a metal, or a metal-like radicle, ith an acidic residue.* The acidic residue is either a halogen p of different elements. Moreover, as the behaviour n when heated (its conductivity), and its behaviour tals (its occlusion), show that hydrogen is to be s a metal, and as the hydroxyl groups of the pond with the acidic residues of salts, acids and e included in the class of salts. Looking at the this point of view, Hittorf made the following

Water is never primarily decomposed when a current is passed through aqueous solutions of electrolytes. Indeed absolutely pure water does not conduct at all. The sulphuric acid added to the water in a voltameter makes the water conduct, is only added because it is known that the acid separates, primarily, into H_2 and SO_4, and that the SO_4 has to then reconverted into H_2SO_4 by its reaction with the water and splitting off oxygen. One ought to speak of this reaction as an electrolysis of sulphuric acid. The addition to the water of some other oxyacid, or of a [illegible] of an alkali salt, makes it conduct, just as the addition of sulphuric acid enables the current to pass.

[illegible] occurring water is to be attributed to the salts in it.

[illegible] observed that the electrolysis of [illegible] follows a somewhat different [illegible] and the intensity [illegible] of one volume of [illegible] is electrolysed, the [illegible] ozone. The [illegible] reactions:

iderable quantities of ozonised oxygen may be ob-
d by using the apparatus represented in figure 10. A
cork is fitted into a small cylinder; the cork carries the
tube for gas, r, a narrower tube, g_1, and a wider tube, R.
wider tube, R, is closed by a cork through which pass
:ube g_2 and also a short narrow tube. The tubes g_1 and g_2
nade of thermometer-tubing: the platinum wires a and k
attached to the lower ends of these tubes by means of
)le glass; these wires project only a short way out of the
:s, and they are soldered to pieces of
per wire which fill the bores of the
:s g_1 and g_2. When the positive pole
a battery of about five accumulators is
nected with the wire in g_1, and the
:ative pole with the wire in g_2, hydrogen
apes by the narrow tube near g_2, and
/gen through r, and the presence of
)ne in the oxygen is detected by the
ie colour which is very quickly produced
the gas is caused to bubble through a
ution of potassium iodide mixed with
.rch paste placed in the beaker-glass.

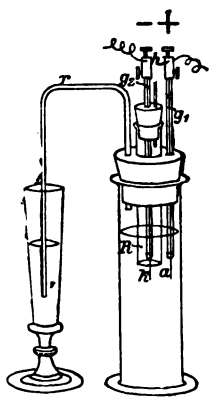


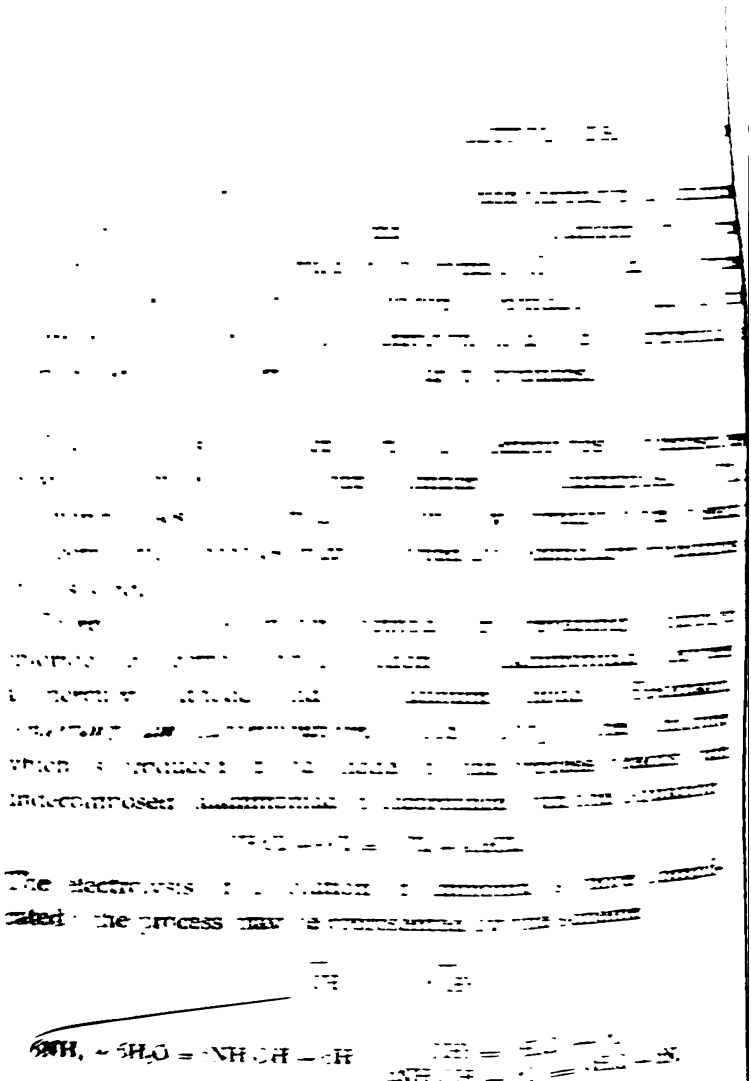
Fig. 10.

tity of ozone increases considerably if some
trioxide is added to the electrolytic liquid, and
:tus is immersed in a freezing mixture.

.perimental arrangement may be used to show the
:n peroxide, besides ozone, during the
.ulphuric acid. Hydrogen peroxide is
anode when the electrolyte contains at
I_2SO_4; the process may be represented

$$+ 2H_2O = H_2O_2 + 2H_2SO_4.$$

:s of hydrogen peroxide are obtained by



$$NH_4 + 4H_2O = NH_4OH + H$$

The radicle NH_4 interacts with water similar to pota-
sium, and six volumes of hydrogen are produced at the
anode. The oxygen which is separated from the KOH
combines with molecules of ammonium hydroxide to
form water, and thus it is that the volumes of
hydrogen produced are in the ratio of 3 to 1.
The current in the apparatus used for

ctrolysis of hydrochloric acid. Inasmuch as the nitrogen is set free dissolves fairly easily in ammonia solution, it to employ as electrolyte a mixture of 250 c.c. concen- solution of common salt and 20 c.c. concentrated nia solution, and to allow the current from six lators to pass through the apparatus for an hour the stopcocks of the two limbs are closed and the k of the upright tube is opened (see fig. 14, p. 33). n an alkaline solution of a lead salt is electrolysed, ygen produced at the anode, as the result of secondary ns, oxidises the lead compound to lead dioxide, as in the following equations:—

$$Pb(NO_3)_2 = Pb + 2NO_3,$$
$$2NO_3 + H_2O = 2HNO_3 + O,$$
$$NO_3)_2 + H_2O + O = 2HNO_3 + PbO_2.$$

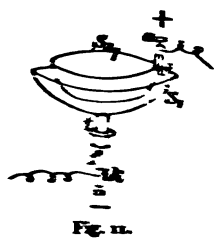


Fig. 11.

periment is easily performed. The asin S_1 (fig. 11), in the tubulus of f, is fastened the short iron wire *f*, d on a triangle, and is filled with r cent. solution of lead nitrate mixed with its own of a normal solution of caustic soda [a normal solution ; 40 grams of NaOH per litre]; a metallic plate, ly a platinum basin, S_2, is immersed in the liquid glass vessel. When *k* has been connected with the pole and *a* with the anode pole of an accumulator, ut fifteen seconds, four or five iridescent, rainbow- l rings of lead dioxide appear on the platinum basin, e art of colouring metals, which aims at ornamenting of copper or brass that have been thinly gilt, is based reaction. The experiment is finished in less than ; if a manganese salt is used the rings of manganese that are formed are more numerous than those of ide. If cobalt sulphate is used instead of manganese

form until after about

silver, by the use of a
$KAgCy_2$), which is such
accomplished, according to
2 Hälfte, p. 74
reactions: the kation
and the anion $AgCy_2$
silver on the

silver from the
cyanide ($AgKCy_2$)
way shown
consists of platinum,
$AgCy_2$, and
cyanide [AgCy]
the separa-
form to
is the result
which gives
double
is separated
primary
which
electrode.
is employed
cyanide is
cyanide
gold
process

its use in 1894 in the Transvaal amounted to about ,000,000, which is an output that places that republic in e forefront of the gold-producing countries at the present ne. The gold, which is found in a very finely divided ndition in the rocks, is dissolved by a dilute solution of otassium cyanide, in the presence of oxidising bodies, in ccordance with the equation

$$4KCy + 2Au + H_2O + O = 2KAuCy_2 + 2KOH;$$

nd the solution is subjected to electrolysis between steel nodes and lead kathodes. Prussian blue, which is again vorked up into potassium cyanide, is formed on he anodes; the leaden kathodes, encrusted with gold, are taken to the furnace-hearths, whereon he gold remains after the removal of the lead by cupellation.

Fig. 12.

The electrolysis of a solution of potassium ferrocyanide, K_4FeCy_6, containing 10 c.c. of a saturated solution of the salt mixed with 200 c.c. of water, and acidified by hydrocyanic acid, shows how complicated the secondary reactions in an electrolytic process may become. The current from five accumulators is passed through the solution placed between platinum electrodes in a U-tube (*see* fig. 12). After about twenty minutes, Prussian blue, $(Fe_2)_2(FeCy_6)_3$, has formed in the anode limb, while the liquid in the kathode limb is milky from small uprising bubbles of hydrogen. According to Hittorf (*loc. cit.*, p. 72), 4K goes to the kathode, where it reacts with water as shown by the equation

$$4K + 4H_2O = 4KOH + 4H,$$

and the ion $FeCy_6$ goes to the anode. If there is a sufficient supply of K_4FeCy_6, the anion reacts with that compound to

according to the

mentioned above, the

of sodium

solution was at each

such as

serves as the

rod x is

edge of the

by cutting

rod of copper

rod x is the

rod x is

connection with a

connected

containing a

rod in F_1.

The current

om five accumulators is sufficient for the experiment. [ydrogen, produced in the secondary reaction

$$2Na + 2H_2O = 2NaOH + 2H,$$

scapes by r_1. According to Jahn (*Grundriss der Elektrochemie*,). 292 [1895]), the following processes take place at the anode:

$$2CH_3.COO + H_2O = 2CH_3.COOH + O,$$

nd $$2CH_3.COOH + O = C_2H_6 + 2CO_2 + H_2O.$$

The gases ethane (C_2H_6) and carbon dioxide (CO_2) escape by r_2; the latter gas is absorbed by the baryta water (the absorption is shown by the formation of a white precipitate of barium carbonate in the flask F_2), while the ethane collects in the cylinder, *Ae*, placed in the pneumatic trough. The volume of ethane collected is almost equal to that of the hydrogen which is obtained in the cylinder *H* placed in the trough on the other side of the electrolytic cell. The deficit in the volume of ethane obtained is due, according to Jahn, to the oxidation of some of the acetic acid, at the anode, by the oxygen in accordance with the equation

$$CH_3.COOH + 4O = 2CO_2 + 2H_2O.$$

The hydrogen and ethane may be distinguished by the luminosities of their flames; or, better, by the fact that the ethane takes fire quietly, while the hydrogen ignites with slight explosion. The experiment is of especial interest in organic chemistry.

It is to be remarked, in concluding this chapter, that endeavours are being made to turn to account the secondary reactions of electrolytic processes between indifferent electrodes for the practical preparation of organic compounds. If a solution of potassium sulphocyanide (1 : 5) is electrolysed, in the apparatus represented in figure 8 (p. 17), by the current from twelve accumulators, hydrogen is given off at the kathode,

while the oxygen at the anode oxidises the sulphocyanic acid to *luteorin*, which is a yellow colouring matter used in dyeing, probably in accordance with the equation

$$6HCNS + 10O + H_2O = C_6H_3O_2N_3S_3 + H_2SO_4 + 2HNO_3.$$

The luteorin soon separates in yellow flocks; and after fifteen minutes enough will be obtained for a dyeing experiment, for which purpose the substance is dissolved in an alkali solution.

Every one knows that iodoform is produced by the reaction of iodine with a solution of sodium carbonate containing alcohol, aldehyde, or acetone. The same compound is formed electrolytically by separating iodine, at the anode, from potassium iodide, under conditions such that the occurrence of a secondary reaction with alcohol in presence of sodium carbonate is possible. The apparatus represented in figure 3 (p. 9) may be used as the electrolytic cell. The tube is filled with a solution of 5 grams potassium iodide and 10 grams sodium carbonate in 100 c.c. of water to which 10 c.c. of alcohol have been added; the apparatus is immersed in warm water in a beaker, and the current from a battery of four accumulators is passed through the bound. After five minutes the smell of [illegible] in the limb which contains the [illegible] unites the bulb of the U-tube is [illegible] iodoform.

[illegible] found an extensive application [illegible] of compounds which are [illegible] the making of aniline [illegible] processes of change [illegible] time and oxidised at [illegible] ver near the kathode. [illegible] in which an acid or [illegible] seems of the case, is

ıbjected to electrolysis. The intensity of the current, the ɔncentration, and the temperature must be regulated in a ɔecial way for each preparation. Nitro-compounds, for ıstance, are reduced to hydrazo-compounds in alkaline ɔlutions, and to amido-compounds in acid solutions.

An example of the oxidising effects of the electric current ɜ furnished by the conversion of aniline into aniline black, in :ccordance with the equation

$$2C_6H_5NH_2 + O_2 = 2H_2O + C_{12}H_{10}N_2.$$

The experiment may be performed by mixing 100 grams of aniline with 100 c.c. of pure hydrochloric acid (spec. grav. 1·119), dissolving 50 grams of the aniline hydrochloride which crystallises out on cooling in 500 c.c. of water, adding 20 grams potassium chlorate, placing this mixture in an electrolytic cell like that used in the experiment illustrative of electrical bleaching (*p.* 12), with a piece of white woollen cloth, which has been boiled in dilute soda solution, stretched on the anode-plate, and sending the current from four accumulators through the liquid; after about thirty minutes those parts of the woollen cloth which are in direct contact with the electrode are coloured greenish black. The electrolytic formation of aniline black may be demonstrated more simply A mixture of 19 grams aniline and 22 grams is neutralised by 24 grams glacial acetic acid; the dissolved in 200 c.c. water, and a few c.c. of this the anode-limb of the U-tube shown s filled to above the electrodes with of common salt. When the current has passed for a few minutes the e-limb become deep black, because ht about by the chlorine which is

CHAPTER II.

FARADAY'S LAW.

THE numerous experiments that have been performed so far have made evident how varying the action of an electrolysing current may be. Once more it must be emphasised that the primary action of the current always is to separate the electrolyte into two parts, one of which parts, that, namely, which is of a metallic character, travels towards the kathode, while the other, which moves towards the anode, consists of the rest of the compound.

It occurred to Faraday, and the idea was a happy one, to send the same current through a series of electrolytic cells arranged one behind the other and containing different electrolytes. It thus became possible to make a quantitative comparison of the changes brought about by the same quantity of electricity in motion. The result of the experiments found expression, in 1833, in *Faraday's law of constant electrolytic action.* In the form given to it by H. von Helmholtz, the law states that *the same quantity of electricity* * *passing through an electrolyte either sets free, or transfers to other combinations, always the same number of valencies.*

The following experimental arrangement is suitable for deducing the law for the kations. In the circuit of the current from five accumulators are included a rheostat, by

* Not to be confounded with the energy of the current.

means of which the current is at first diminished, a Hofmann's apparatus for the electrolysis of water, and four glass troughs: the Hofmann's apparatus and two of the troughs are represented in figure 14. The electrode-plates *a* and *k* project downwards in each trough; the conducting wires of these plates are connected by binding screws with the slips of copper *S S*. The kathodes are composed wholly of platinum; they must be cleaned carefully, by fuming nitric acid, and weighed, accurately to a centigram, before the experiment begins. Either platinum, or the metal which is contained in the electrolyte, may be used for making the anode in each cell. In selecting electrolytes, care must be taken that the metals deposited on the kathodes, *shall* adhere firmly to the platinum plates, that these deposited metals shall not suffer oxidation, at any [illegible] ot during the time requi[illegible] veighing, and that the [illegible]cies of the atoms of the [illegible] shall be as different [illegible] fol-

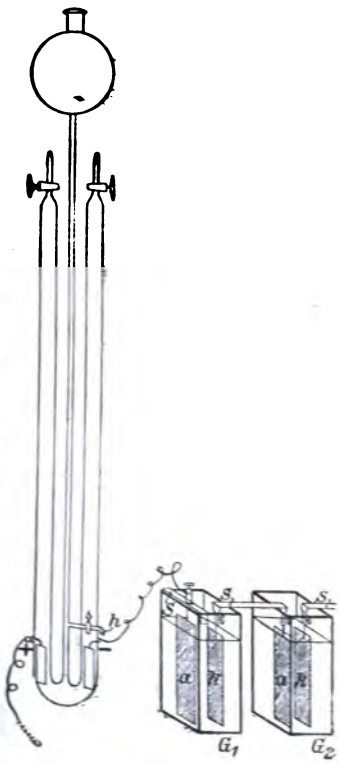
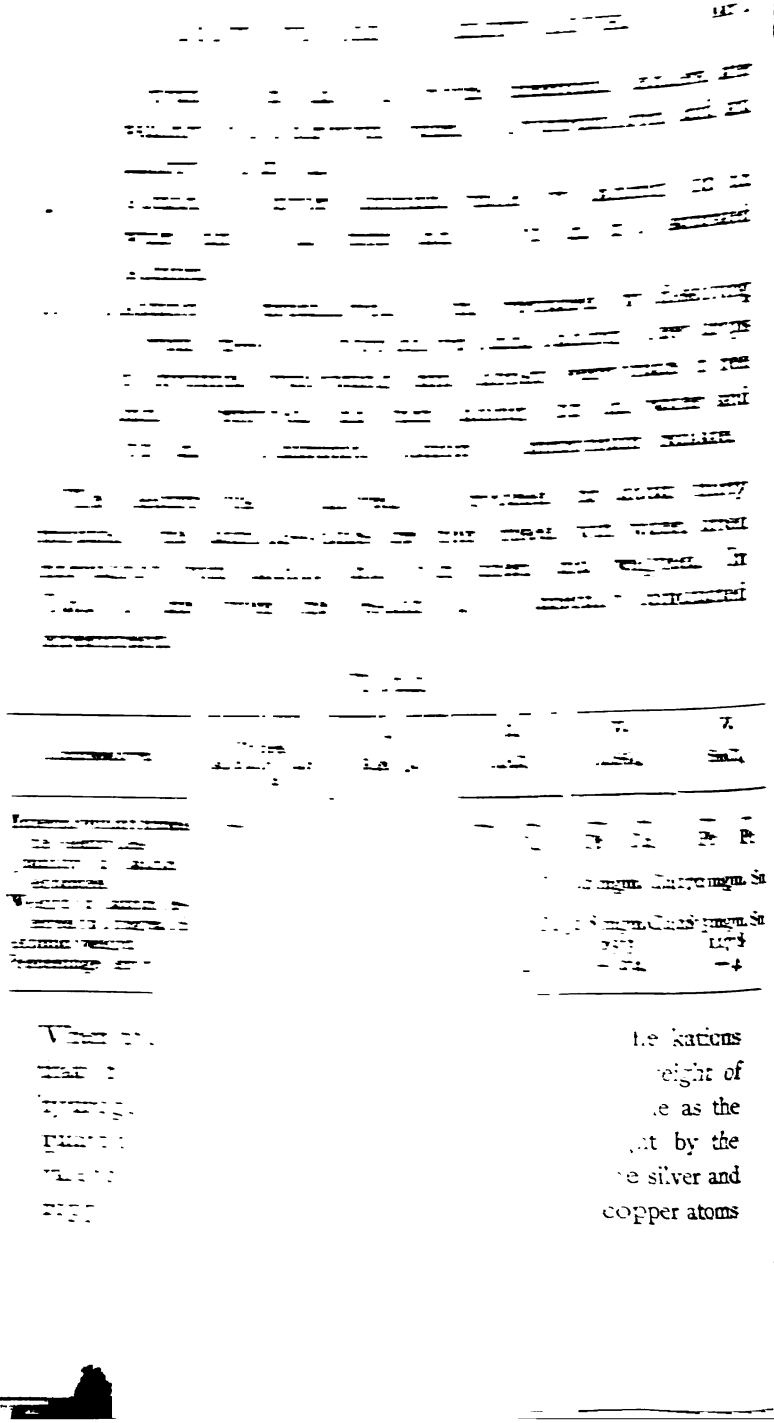


Fig. 14.

lowing [illegible] recommended:—

(1) A [illegible]-silver cyanide, obtained by dis-[illegible]er nitrate and 5 grams potassium [illegible]ater.

[illegible] chloride, prepared by dissolving



are divalent, and in column V. the atoms of tin are tetravalent. The law of Faraday is demonstrated satisfactorily by the experiments. Moreover, the results show that the quantities of the kations that have been separated are proportional to the quantity of the current, and also to the duration of the action of the current.

The more accurate experiments of F. and W. Kohlrausch have shown that 0·3281 mgm. of copper was separated from cupric salts by one *coulomb** of electricity; or, that 31·65 grams of copper were separated by 96,465 (in round numbers 96,500) coulombs. This quantity of electricity expresses the *electro-chemical equivalent*, that is to say, the number of coulombs which causes the separation, in one second, of that fraction of the atomic weight of a metal, or of the [formula-] weight of an anion-group, expressed in grams, which corresponds with a single valency.†

The measurement of the intensity of a current [that is, the quantity of electricity which passes through any cross-section of the conductor in one second] by means of voltameters depends upon the exact proportionality between the quantity of electricity and the quantity of the ions that are separated. One coulomb separates 1·1181 mgm. silver, per second, in a

* If the unit of electricity, one *coulomb*, flows through any conductor in one second, the intensity of the current ... of potential, the *volt*, is so fixed that one coulomb ... it, per second, through a resistance of one *ohm*, ... of mercury 106·3 centims. long and 1 sq. mm. ... so adjusted that 1 coulomb × 1 volt, that ... is equal to the work of 10^7 *ergs*. This ... *t*.

† ... may be put thus. The electro-chemical ... coulombs that causes the separation of a ... or anion-group, in one second; a gram- ... obtained by dividing the atomic weight of ... ht of the anion-group, taken in grams, by ... ion-group.—[TR.]

silver-voltameter, and sets free 0·174 c.c. explosive gas [hydrogen and oxygen in the ratio of 2 to 1 by volume] reduced to 0° and 760 mm. pressure] in the same time in a water-voltameter. Supposing that 10 c.c. hydrogen and 10 c.c. oxygen referred to normal temperature and pressure) were obtained, in an apparatus for electrolysing water, in three minutes, this is equal to a production of 0·1667 c.c. explosive gas per second, and, therefore, the quantity of electricity was

0·1667 / 0·174, that is 0·958 coulomb.

If one has three apparatuses of nearly equal size for the decomposition of water, whose resistances are equal (say 10 ohms each), then the law of the division of the current may be experimentally deduced in a few minutes by using the arrangement shown in

Fig. 15.

...raun, *Die Elektricität und ihre Anwendungen*.

B is a battery of twelve accumulators; the ... the current-path ... amounts to ... the resistance ... in the current-path ... In a ... ment there were obtained ... c.c. ... two volumes hydrogen with one ... c.c. in ... and ... c.c. in ...

where the quantity of the current passing by the path $b\,B\,A_1\,a$ is represented by i_1, the quantity passing along the path $a\,A_2\,w_2\,b$ is represented by i_2, and i_3 is the quantity passing by the path $a\,A_3\,w_3\,b$. If the resistance of one of the decomposition-apparatuses is expressed by W (the three have all the same resistance), then the equation ought to hold good

$$i_2\,(w_2 + W) = i_3\,(w_3 + W).$$

The equation is fairly satisfied by the experimental results; for $i_2\,(w_2 + W) = 379{\cdot}5$, and $i_3\,(w_3 + W) = 352{\cdot}5$. The difference between these values is due to differences between the decomposition-apparatuses A_1, A_2, and A_3.

It follows from Faraday's law that when a quantity of electricity measured by 96,500 coulombs acts on an electrolyte, such quantities of the ions as correspond with a single valency always travel towards the electrodes where the respective actions take place, independently of the chemical affinity whereby these ions are bound together in the undecomposed molecules. The accuracy of the law has been established by H. von Helmholtz even for a current so feeble that a century would be required for it to separate a single milligram of explosive gas from water.

In the *Faraday Lecture* delivered by him in London on April 5th, 1881 [see *Journal of the Chemical Society*, **39**, p. 277], H. von Helmholtz laid the foundations of a new electrochemical theory which explains the facts embraced by Faraday's law.

The most important of these facts may be stated thus:

F. ...*gle valency of an elementary or compound ion is charged* ...*he same quantity of positive or negative electricity,* ...*es as if it were an electrical atom that cannot be* ...*ded.* When, therefore, the circuit is closed, the ... the electrolytic cell, being charged positively, ar...

attracted to the kathode, and the negatively charged anions are attracted to the anode. If it is then possible for the ions to be set free, this does not occur throughout the whole mass of the electrolyte, but always only at the electrodes, and it is brought about by those quantities of electricity of opposite kinds which are carried to the electrodes by the current neutralising one another.* The result is that the ions cease to be in the ionic condition. This happens in the separation of the heavy metals on the kathode. But if the anion causes solution of the material of the anode to take place, that is to say, if it brings that material into the ionic condition, then a quantity of the metal of the anode, which quantity depends on the valency of that anion, becomes charged positively at the expense of the current. For instance, if the SO_4 ion dissolves one atom of copper from a copper anode, two positive charges are used, and the copper atom becomes a copper ion. When, therefore, a solution of copper sulphate is electrolysed between copper electrodes, the current produces new kations by charging the atoms of the metallic copper at the anode, and an equal quantity of positive electricity is given up at the kathode whereby the kations are un-ionised and become metallic atoms. If the ions react with the water, then negative hydroxyl ions are formed at

* The words used by von Helmholtz are these: "The same definite quantity of either positive or negative electricity moves always with each univalent ion, or with every unit of affinity of a multivalent ion, and accompanies it during all its motions through the interior of the electrolytic fluid. This quantity we may call the electric charge of the atom. . . . If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions, which behave like atoms of electricity. As long as it moves about in the electrolytic fluid, each ion remains united with its electric equivalent, or equivalents. At the surface of the electrodes decomposition can take place if there is a sufficient electromotive force, and then the ions give off their electric charges and become electrically neutral" (*loc. cit.*, pp. 289-90).—[TR.]

the kathode, and positive hydrogen ions are formed at the anode, from the molecules of water, at the cost of the electrolysing current. Consequently, when the anion SO_4 appears at a platinum anode, two positively charged atoms of hydrogen, and also an atom of oxygen, are set free from the molecule of water; and when a potassium ion, or a sodium ion, appears at the kathode, a single hydroxyl group becomes negatively charged at the kathode, and this group plays the part of the anion necessary to the alkali ion, while an atom of hydrogen is disengaged at the kathode.

H. von Helmholtz has thus made clear wherein consists the process of the passage of electricity through a conductor of the second class, which must always be a chemical compound. At the same time, by the hypothesis that equal quantities of electricity cling to ions of equal valency, he has explained why the weights of the substances that are concerned in those chemical changes which are brought about by equal quantities of current electricity are always in the ratio of the equivalent weights of these substances. Moreover, it is possible to understand how isomeric ions can differ qualitatively, for instance in their colours; why the ferro-ion should be green while the ferri-ion is yellowish red, or why the MnO_4 ion of permanganic acid ($HMnO_4$) is violet and the MnO_4 ion of manganic acid (H_2MnO_4) is green. The qualities of the ions are dependent on their energy-content, and this, in turn, is conditioned by the number of the valencies, and consequently also by the number of the electric charges. (For more details see Chapter V.)

The positive charge on a hydrogen ion can be calculated approximately by considering that 1 mgm. of hydrogen is separated by 96,465 coulombs, and by making the assumption, which is based on definite facts, that this quantity of hydrogen consists of $1{\cdot}2 \times 10^{21}$ atoms. Hence a hydrogen

ion must be charged with coulombs $(1.2 \times 10^{-4}) = 8 \times 10^{-20}$ coulombs $= 8 \times 10^{-1}$ absolute units: this quantity may be taken to represent the absolute charge of a single valency.

It is certainly still doubtful how the details of the process of the neutralisation of ions at the electrodes are to be pictured in the mind. Two opinions exist. Either the ion becomes actually deprived of electricity when it has given up its proper charge, or it is furnished with a charge of the opposite kind in consequence of the use at the electrode of the double quantity of charge, and then it unites with an unchanged ion to form a molecule consisting of two oppositely charged atoms (for instance, $\overset{+}{H}\ \overset{-}{H}$). The latter hypothesis is hard to reconcile with the generally acknowledged monatomicity of the metallic molecules, and it tends on the whole to the final identification of electrical and chemical energy, an identification which was made years ago by Berzelius. But as our knowledge of the nature of the two forms of energy is still very defective, it seems better to adopt the first hypothesis, which, moreover, is the simpler of the two, and has already been employed in the explanations that have been given.

CHAPTER III.

HITTORF'S TRANSPORT-NUMBERS.

WHEN a current which is not very strong passes through a solution of copper sulphate, for a long time, between copper electrodes placed vertically, no further change seems to take place beyond the travelling of the copper with the positive current from the anode to the kathode; the anode loses as much copper as the kathode gains. Nevertheless, if the electrodes are connected with a galvanometer after the passage of the current, a polarisation-current is observed in the direction opposite to that of the primary current. Now the polarisation-current cannot be caused by gases, as is the case in the electrolysis of dilute sulphuric acid between platinum electrodes, for gases do not appear on these electrodes if the primary current is made sufficiently weak. The primary current must, therefore, have caused changes of some kind in the copper sulphate solution itself which give rise to the polarisation-current. It was soon discovered that the changes in the copper sulphate solution consisted in an increase of the concentration of the solution at the anode and a decrease at the kathode, while the total quantity of copper sulphate in the solution remained constant.

In the years 1853-59 Hittorf made a study of a great many cases of those changes which occur in the concentrations of electrolytes at the electrodes. Hittorf's papers *Über die*

Wanderungen der Ionen are collected in Nos. 21 and 22 of *Ostwald's Klassikern*. The results of his laborious investigations were not properly appreciated until recently.

The decomposition-cells used by Hittorf were constructed so that the electrodes lay horizontally over one another, and the solution could be removed after the electrolysis in layers, without the risk of getting mixed, and each of these layers could then be analysed separately.

These changes of concentration can easily be made visible by means of the apparatus shown in figure 16. A piece of glass tubing, 50 centims. long and 3 centims. diameter, is closed at both ends by corks through which pass the thick conducting wires *a* and *k*, and these wires are soldered to perforated, sieve-like plates of copper. If the poles of a battery of five accumulators are attached to the conducting wires, and a rheostat is included in the circuit by means of which the intensity of the current is so reduced that gas is not given off, the liquid which surrounds the kathode, *k*, becomes quite colourless after some minutes.

The changes of concentration calculated from the data in one of Hittorf's experiments are represented by the device in figure 16. To make the illustration clearer, the percentage numbers are expressed by the corresponding numbers of ions, [illegible] being represented by the white dots and the [illegible] the black dots. The horizontal line separates the [illegible] the kathode from that around the anode. The [illegible] homogeneous before electrolysis begins, and we may [illegible] and 6 anions are present in each [illegible] has been passing for a certain time, [illegible] ited on the kathode, and an equal [illegible] is dissolved by the SO_4 ions. [illegible] Cu and 5 SO_4 are found on the [illegible] 7 SO_4, besides the 6 re-formed

$CuSO_4$, are found on the anode side. If there were only a wandering of the anions during electrolysis, there would be $9 + 6 = 15$ $CuSO_4$, in all, in the anode layer, and there would, therefore, be $9 - 6 = 3$ $CuSO_4$ in the kathode layer. If, on the other hand, only 6 Cu ions had travelled from the anode layer to the kathode layer, to the 6 SO_4 ions that had there become free, then there would have been 9 Cu and 9 SO_4 in each layer as there was before electrolysis began. As a matter of fact, 5 Cu and 5 SO_4 are found at the kathode, and $7 + 6$ Cu and $7 + 6$ SO_4 at the anode. Both kinds of ions have been transported, the Cu ions towards the kathode and the SO_4 ions towards the anode, and, moreover, 2 Cu have moved from beneath upwards and 4 SO_4 from above downwards. Six copper atoms being set free at the kathode, 2 Cu ions move upwards, while the 4 remaining free SO_4 ions move downwards, so that there are, in all, 6 free SO_4 ions under the line, and these are provided with Cu ions at the cost of the anode. It may be said that a Cu ion will pass over two of six spaces, and a SO_4 ion will pass over four in the same time. The quotients $\frac{2}{6} = 0{\cdot}33$ and $\frac{4}{6} = 0{\cdot}66$ are called by Hittorf the *transport-numbers* (*Zahlen der Überführungszahlen*) for the kation Cu and the anion SO_4, respectively. These numbers express the quantities of both ions transported for each copper atom that is separated; or may be taken to represent the distance passed over by each ion, divided by the sum of the distances traversed by both ions.

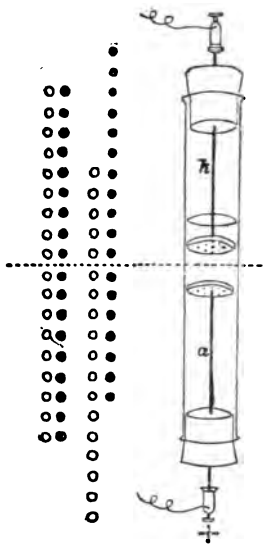


Fig. 16.

If the transport-number of the anions is expressed by n, that of the kations is $1-n$. The ratio $(1-n) : n$ must evidently be the ratio of the velocities, u and v, of the kations and anions under the influence of the difference of potential at the electrodes. Consequently the equation holds good

$$\frac{1-n}{n}=\frac{u}{v}$$

Hittorf's researches have shown the ratio u/v to be independent of the differences of potential at the electrodes, and also, within certain limits, independent of the concentrations of the solutions. The effect of temperature has shown itself to be inappreciable, if the experiments are made at about ordinary temperatures. But at higher temperatures the difference between u and v decreases more and more.

CHAPTER IV.

THE LAW OF KOHLRAUSCH.

IN his communications on the migrations of the ions, Hittorf repeatedly drew attention to the possibility of obtaining fuller insight into the nature of electrolysis by making measurements of the *specific conductivities* (that is, the reciprocals of the resistances) of electrolytes. But it was a long time before a practicable method for measuring the resistances of electrolytic solutions could be found, because gases are generally produced by the passage of the current through these solutions, and those gases give rise to an opposing electromotive force the magnitude of which is subject to variations.

F. Kohlrausch discovered a method in 1880. The principle of his method is the same as that which is applied to the measurement of the resistances of wires by the use of Wheatstone's bridge. The influence of polarisation is eliminated by the employment of an alternating current from an induction-machine, and a telephone is used as indicator in place of a galvanometer. The solution under examination is placed in cell between platinised platinum electrodes [that is, platinum tes covered with a fine coating of platinum black, by olysing a very dilute solution of platinum chloride ween them].

The method of measurement is represented diagram-

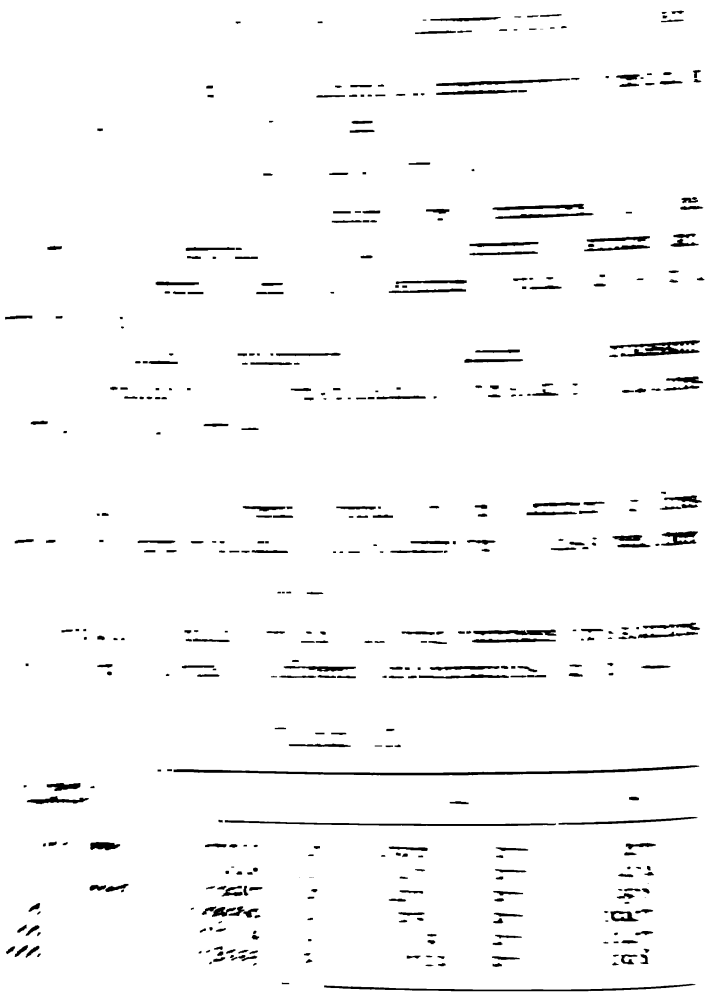
; and in column 5

are given the increases of conductivity (Δl), per degree of temperature, in percentages of l.

TABLE II.

ELECTROLYTE.	p.	r.	l.	Δl.
H_2SO_4	5	4·8	195	1·21
,,	30	1·4	691	1·62
HCl	5	2·5	369	1·59
,,	10	1·6	590	1·57
,,	20	1·3	713	1·55
,,	30	1·5	620	1·53
NaCl	5	15·0	63	2·20
,,	10	8·3	113	2·10
,,	15	6·1	153	2·10
,,	25	4·7	200	2·30
NaOH	17	2·9	326	—
$CuSO_4$	5	53·3	18	2·20
,,	10	31·4	30	2·20
Mercury . .	. . . .	0·0000943	10,000,000	
Copper . .	. . . .	0·0000017	550,000,000	

Now, just as in the case of Faraday's law, so in the present case, it was not to be supposed that a law to express the conductivities of different electrolytes could be arrived at as long as the concentrations of the solutions were stated merely in percentages; Kohlrausch, therefore, referred the values of L to equimolecular solutions, and so obtained the *molecular conductivities* λ. An example will make the conception of molecular conductivity more intelligible. The specific resistance, s, of a solution of potassium chloride containing 5 grams of the salt in 100 c.c. was found to be 160,256 in mercury units at 0°. Hence $L = 62{\cdot}4 \times 10^{-7}$. As 5 grams of potassium chloride are contained in 100 c.c. of the solution, one gram-molecule, that is 74·5 grams [KCl = 74·5], would be contained in 1490 c.c. of an equally concentrated solution. It follow



[illegible] specific conductivity of an [illegible] concentration decreases, but that the [illegible] decreases as rapidly as the concentra- [illegible] value for $I_{\frac{1}{10}}$ is more than a tenth [illegible] part of a thin column of a [illegible] to this original length of the column

by the addition of pure water, the conductivity after dilution would be not exactly one-tenth, but more nearly 0·11, of the conductivity of the original column before dilution. Although only a tenth part of the original quantity of salt is present after dilution, nevertheless that tenth part of the salt is affected by the greater dilution in such a way that it conducts the current better than one would have expected; or, to use the language of the theory of Arrhenius, which will be considered in Chapter V., the relative number of *active molecules* has increased. The same thing finds expression in the values of λ given in the table. The following statement is deduced from these values:—

The molecular conductivity of an electrolyte increases with the dilution, and at a definite limit it reaches the maximum value λ_{∞}.

The maximum values can be calculated from the experimental data by the method given by Ostwald.* For potassium chloride the maximum value is 140.

By comparing the values of λ for very dilute solutions of two electrolytes with the same anion and different kations, on the one hand, and two electrolytes with another common anion and the same two kations as the previous pair, on the other hand [for instance, by comparing the values of λ for very dilute solutions of KCl and NaCl with the values

* The method is based on the fact that, so far as experiments have gone, every ion can be combined with another ion of such a nature that the maximum conductivity of the salt so produced is attained at a workable temperature. Sodium is the kation most generally employed, because solutions of all salts of sodium attain their maximum conductivities at dilutions within the limits of experimental error. And NO_3 is the most ral[illegible]y used anion, as the maximum conductivities of nitrates in solution [illegible]ched at workable dilutions. (*See* Ostwald's *Lehrbuch der allgemeinen Chemie*, vol. ii. (Part I.), pp. 673-4; also the article "Physical [illegible]thod[illegible]" in Watts' *Dictionary of Chemistry*, new edition, vol. iv., p. 92.)—[TR.]

			58·5	71·4
			53·3	6·4
			45·6	74·4
			44·0	69·7
			58·5	58·7
			59·2	65·0

These numbers show that $\lambda_{KCl} - \lambda_{NaCl} = 140 - 120 = 20$, and $\lambda_{KNO_3} - \lambda_{NaNO_3} = 135{\cdot}7 - 113{\cdot}7 = 22$. The differences are nearly the same. Now if the hypothesis of Kohlrausch is correct, if the formula $\lambda_\infty = u + v$ always holds good, the value of λ_∞ found empirically for one electrolyte must agree with the sum of the mean values for u and v, which are calculated from empirical data for n and λ_∞ for other electrolytes. The value of v_{NO_3} for the electrolyte KNO_3 is 67·4, and the value of u_{Ag} for $AgClO_3$ is 58·5; hence $u_{Ag} + v_{NO_3} = 125{\cdot}9$; the actual determination of λ gave $\lambda_{AgNO_3} = 124{\cdot}2$, which agrees well with the calculated value. The formula $\lambda_\infty = u + v$ is thus the expression of a law. The law is called *the law of the independent migration-velocities of the ions.*

The following mean values have been determined by Kohlrausch (*Wied. Annalen*, **50**, p. 385 [1893]); the temperature was 18°.

For K	$u = 60$	For Cl	$v = 62$
„ Na	„ $= 40$	„ NO_3	„ $= 58$
„ Ag	„ $= 52$	„ ClO_3	„ $= 52$
„ H	„ $= 290$	„ OH	„ $= 165$

Solutions of medium concentration of normal salts formed of two monovalent ions give results which are in close keeping with those demanded by the law of Kohlrausch, as do also certain strong mono-acid bases and monobasic acids. But the experimentally determined molecular conductivities of electrolytes with polyvalent ions are smaller, even when working with very dilute solutions, than the values required by the law; Ostwald has, therefore, given the following more general form to the law,

$$\lambda = a(u + v),$$

a has the value of a proper fraction. The experimental which it must be confessed are very meagre as yet,

[illegible]

[illegible]

[illegible]

passed first through the sodium acetate solution, and then through the solution of common salt, the same U-tube being used. The needle shows a deviation in the latter case about three times greater than in the former, and this is due essentially to the greater velocity of migration of the chlorine ion in comparison with that of the anion $C_2H_3O_2$.

The second experiment furnishes an objective representation of the differences of ionic velocities. Figure 18 represents the principle of the arrangement devised by Lodge (*British Association Reports*, 1887, p. 389) for the direct ascertainment of

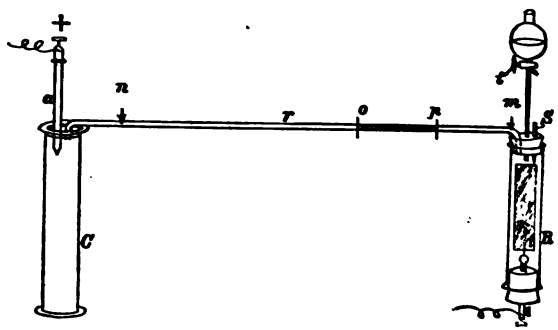
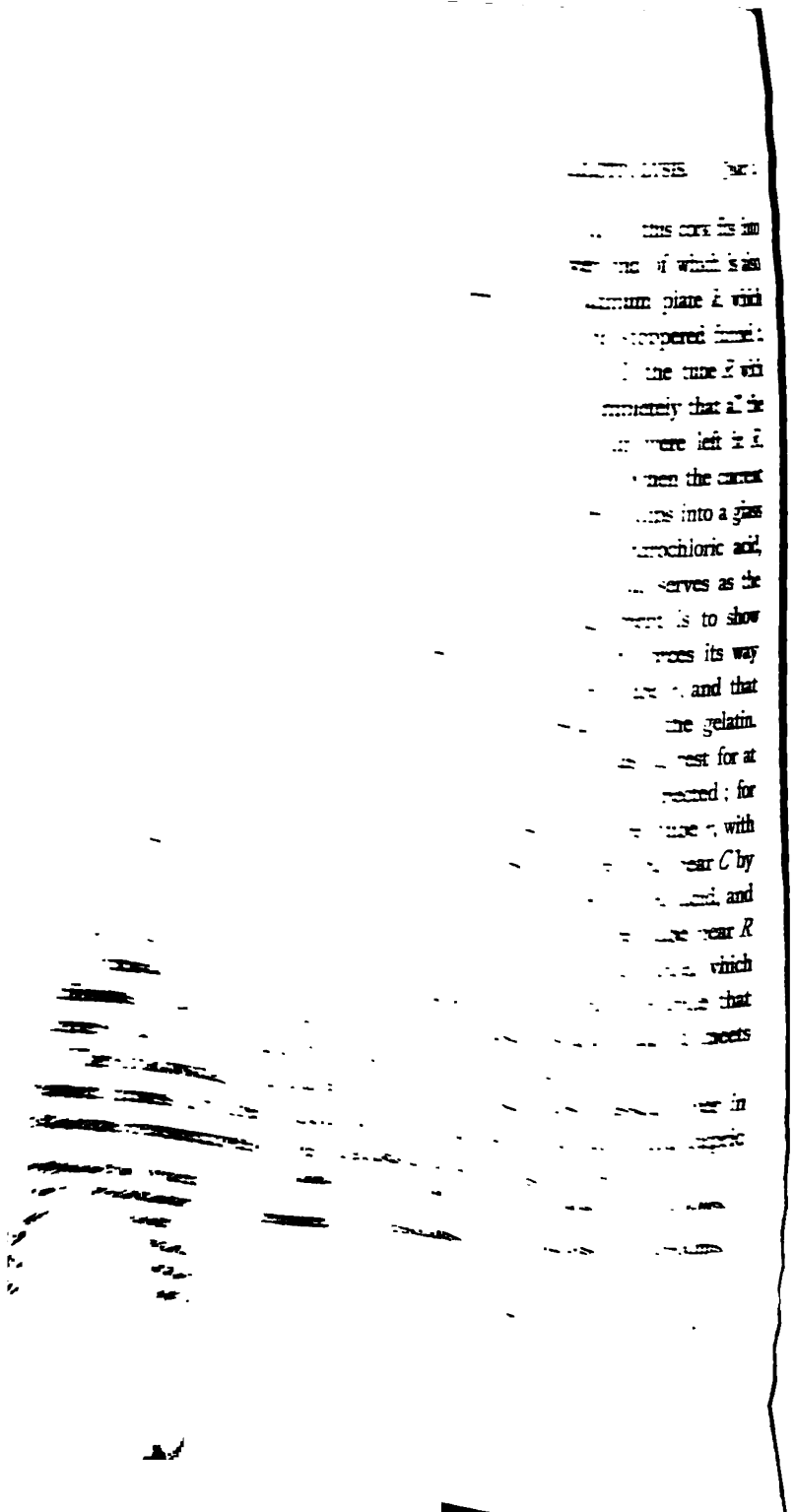


Fig. 18.

the velocities of the migration of ions; the apparatus figured here is copied, with some changes, from that used by him. A centimetre scale is cut, by a diamond, on a piece of glass tubing, *r*, 40 centims. long and 8 mm. wide, and the tube is bent, at right angles, at 1½ centims. from either end. Ten grams of pure gelatin are heated with 140 c.c. of water on a water bath until the gelatin is dissolved; 7 grams of pure sodium chloride, a few drops of a slightly alkaline solution of phenol-, are then added, and the whole is thoroughly mixed ed through paper, and the rose-pink filtrate is poured tube *r*, where it soon solidifies. One end of the tube ssed through a cork, which also carries a stoppere



These numbers agree with the law of Stefan: $h = a\sqrt{t}$, where h is the distance passed over by the diffusing liquid in the number of hours t, and a is a constant. For dilute hydrochloric acid $a = 1$, and for the cupric chloride solution $a = \frac{1}{2}$.

After twenty-five hours, and when the gelatin in the part of the tube mn is still rose-pink, a battery of ten accumulators is connected with the electrodes. The process of decolourisation now proceeds unequally. While the chlorine ions and the copper ions are un-ionised at a and k, and the current is thus allowed to pass through the apparatus, the hydrogen ions of the hydrochloric acid travel from a towards k, and the chlorine ions of the cupric chloride travel from k towards a; in two hours the hydrogen ions move over a space of 3 centims., and the chlorine ions over a space of 0·5 centim. The movements of these ions are attended by the decolourisation of the gelatin. After ten hours only the little part op remains red; the decolourisation has spread in this time to a distance of 18·8 centims. from the anode, and to 3·7 centims. from the kathode (the gelatin in the space mp is no longer blueish and turbid, but it is as colourless as in no). The red zone at last quite disappears, between the marks 31 and 32.

The decolourisation which is brought about by the current is due to the combination of the hydrogen ions, that come from the anode, with the hydroxyl of the base that is present in the gelatin, whereby water is formed, while the sodium atoms that remain over combine with the chlorine ions that approach from the kathode, and so produce a neutral salt. It thus comes about that, as the ions travel through the gelatin, the alkali is removed at both sides, and the phenolphthalein becomes colourless.

The decolourisation of the gelatin would have been accomplished by the diffusion process alone, in the time during which the current has been allowed to pass, to the distance

CHAPTER V.

THE DISSOCIATION THEORY OF ARRHENIUS.

IN 1887 Svante Arrhenius put forward his *theory of the electrolytic dissociation of ions*, and thereby gave an explanation which might be accepted of those phenomena of electrolytic conductivity which had been summed up by Ostwald in the general formula $\lambda = a\,(u+v)$.

As the law of Kohlrausch tells that, under the influence of the electric current, the ions travel with definite velocities dependent on their chemical natures, and as it must be a matter of indifference which anion belongs to a determinate kation, Arrhenius asserted that *the molecules of electrolytes in aqueous solutions are already dissociated into their two ions which are loaded with their respective electric charges*; that electrolysis does not, therefore, require the previous splitting of the molecule by the electric current. While under ordinary conditions the ions move irregularly to and fro among the water molecules, and one ion will sometimes approach and sometimes recede from an ion of the opposite kind, if a difference of potential is established between the electrodes immersed in the solution, then, according to Arrhenius, the ions follow definite paths, the kation goes towards the kathode and the anion towards the anode, and they also move more quickly. The first work which the electrolysing current has to do is to overcome the frictional resistances experienced by

the ions from the water molecules which stand in their way. These resistances vary in accordance with the nature of the ions, and the greater they are the smaller is the mobility of the ions, and therefore the smaller their migration-velocities. These electrolytic frictions are very considerable, according to Kohlrausch (*Wied. Annal.*, **50**, p. 407). To drive forward a gram-ion, in dilute solution, with a velocity of 1 centim. per second, requires a force equal to the weight of 984,000 / (E . U) or 984,000 / (E . V) kilograms, where E is the equivalent weight of the ion, and U, or V, is the velocity of migration of the kation, or anion, in absolute units (see end of last chapter). For 39·1 grams potassium, in dilute solution, would be required a weight of $984{,}000 / (39{\cdot}1 \times {\cdot}00066) = 38 \times 10^6$ kilograms. This very considerable quantity of work, which is used for the transport of the ions, and which forms a substantial part of the energy that is brought into the solution by the current, is transformed into heat; just as a portion of the current-energy, depending on the specific resistance of the conductor, is changed into heat in a metallic conductor.

But if the current is to pass continuously through an electrolyte it must perform a second portion of work at the electrodes; it must neutralise the ions that are attracted to the electrodes, either by drawing away the charges that cling to them with a definite intensity, or by forming new ions from the material of the electrodes or from the water, new anions for the kations and new kations for the anions.

Accordingly, the passage of a current through an electrolytic liquid is dependent on the presence of free ions in the liquid, and any undissociated [non-ionised] *molecules that may be in the liquid take no part in the carrying of the current.*

In the formula $\lambda = a\,(u+v)$, the factor a expresses what fraction of the theoretical value $\lambda\infty$ the experimentally determined value λ actually is. But in the dissociation theory

acquires a more definite meaning. As the passage of the current is due altogether to the free ions, α expresses the fraction of the total number of molecules of the electrolyte which has undergone dissociation; α is, therefore, called *the dissociation-coefficient* [or *ionisation-coefficient*].* If, for instance, 100 gram-molecules of the electrolyte are dissolved in one litre of water, and 80 gram-molecules are dissociated, then $\alpha = 0{\cdot}8$. The remarkable fact that the value of λ increases as dilution increases, that is to say, the conductivity of the same quantity by weight of the electrolyte increases, is explained by Arrhenius by supposing that the continual addition of the solvent brings about the dissociation [or ionisation] of more molecules of the electrolyte, and therefore the production of more ions available for the carrying of the electricity. Arrhenius has expressed this view by saying that the number of *active molecules* is increased. If all the molecules are dissociated [or ionised] at a definite dilution, then the conductivity reaches its maximum at that dilution, and is expressed by the symbol λ_∞. In this case $\alpha = 1$.

From the equations $\lambda = \alpha(u + v)$ and $\lambda_\infty = u + v$, it follows that

$$\alpha = \lambda/\lambda_\infty .$$

Such chemically pure liquids as condensed hydrogen chloride or 100 per cent. sulphuric acid do not conduct, because, according to the dissociation theory, their molecules are not ionised. For the same reason chemically pure water is not an electrolyte; for the water purified by Kohlrausch and Heydweiller, and distilled in a vacuum, showed a specific resistance at 18° of

* It seems distinctly better to use the terms *ionisation*, and *ionisation-coefficient*, rather than dissociation, and dissociation-coefficient. Dissociation has always been thought of as a process of separation of molecules into atoms, or atomic groups, such that the products are unconnected by any chemical bonds and can be separated from one another by diffusion. —[TR.]

$2{\cdot}475 \times 10^{10}$ mercury units (*Sitzungsberichte der K. preuss. Akad. physik.-math. Klasse*, 1894, p. 395). A column of that water 1 mm. high would oppose a somewhat greater resistance to the passage of a current than that of a copper wire of equal thickness stretched three hundred times round the equator. The molecular conductivity of a litre of that water would be $0{\cdot}404 \times 10^{-4}$; and, as $\mu_H = 290$ and $\mu_{OH} = 165$, the dissociation of the water would be so small that 1 gram H ions and 17 grams OH ions would be contained in 12½ million litres.

Water as pure as this may, therefore, be regarded as a non-conductor; and it may be taken for granted that the water in a solution does not take a primary part in the electrolysis of the solution.

The circumstance that the most carefully distilled water is not a perfect non-conductor is due, according to the accurate observations of Warburg (*Wied. Annal.*, 1895, p. 396), to the presence of very minute quantities of impurities which are electrolytes, and which are extremely difficult to remove. The very small conductivities which are always found to be exhibited by such organic compounds as aniline, xylene, and turpentine-oil, however carefully the compounds may be purified, are to be assigned to a similar cause. Warburg recommends the removal of impurities of this kind by electrolysis, a process whereby the compounds are *purified electrically*.

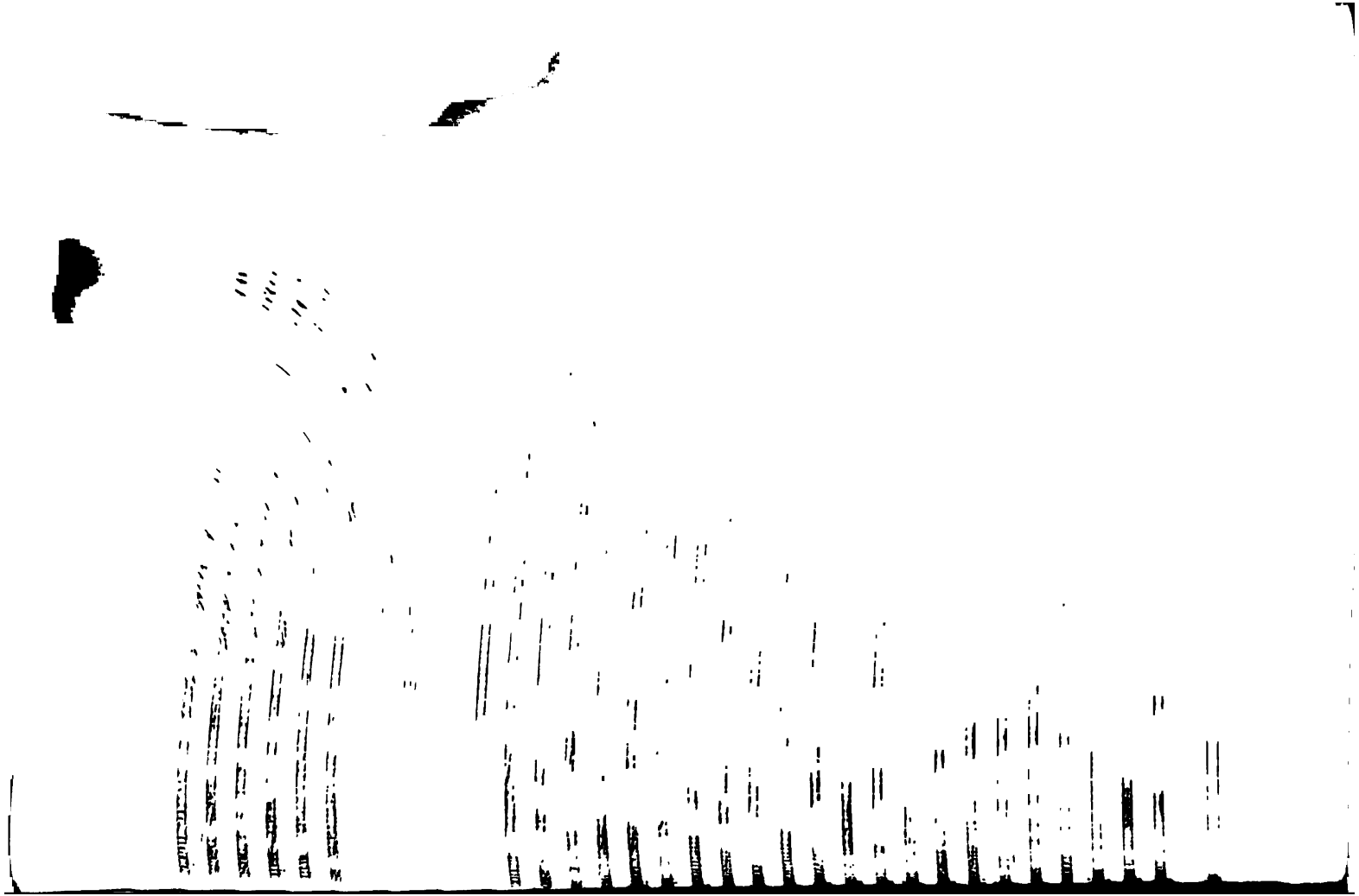
In face of the facts that neither any simple electrolyte, nor pure water, conducts the current, it is extremely remarkable that aqueous solutions of these electrolytes should allow the current to pass. The water must be looked on as able to separate the molecule of an electrolyte into its two ions, and therefore to overcome the forces by which the ions are held together [illegible] molecule which appears neutral when viewed [illegible] About. As the occurrence of the purely physical process [illegible] dissolution of an electrolyte is generally accom-

anied by the disappearance of heat, it is probable that this ocking up of energy is connected with the work of dissociation. For instance, 8500 gram-calories, corresponding with 3600 ilogram-metres of work, are locked up during the dissolution f 1 gram-molecule (101 grams) of potassium nitrate. We ave not as yet been able to penetrate further into the details f the mechanism of dissociation [that is, of the ionisation of electrolytes in aqueous solutions].

There are certain other liquids, besides water, which are able to cause the dissociation of electrolytes dissolved in them; these liquids are compounds, like alcohol, which contain hydroxyl groups. Water, however, greatly surpasses all these liquids in its power of bringing about dissociation, and it is because of this, as well as because of its other exceptional properties, that water plays so important a part in the economy of nature.

While a solution of hydrogen chloride in water is an excellent conductor, the passage of a current, even a current of considerable intensity, is completely stopped by a solution of the same compound in chloroform. For, if a solution of dry hydrogen chloride in chloroform is placed in a U-tube (*see* fig. 12, p. 27) fitted with platinum electrodes, which are connected with a battery of ten accumulators, the needle of a galvanometer included in the circuit will not show the slightest deviation. The absence of ions in this solution is also the reason why litmus paper is unchanged when it is immersed in the liquid; it is only after water has been added that the litmus is reddened.

There are certain aniline colouring-matters which behave towards water and towards other solvents similarly to hydrogen chloride. A very little [of the potassium salt of] *eosin*, $C_{20}H_6Br_4O_5)K_2$, is shaken with a mixture of 20 c.c. ether and c.c. alcohol, and the liquid is poured through a filter of the



suffices to reverse the dissociation, for the hydrochloric being much more easily dissociated than the violuric takes away the water from the latter.

The conductivity of electrolytes when fused can be understood, in so far as the heat used for melting also takes part in the work of dissociation.

There is, however, still a question to answer, and it is this: whence are the electric charges of the ions, those constituents of the molecule of an electrolyte, derived? When the ions are not elementary atoms do they form themselves from such atoms, and must we think of these atoms as in themselves unelectrified?

These questions are not yet decided. The first step towards a solution has, however, been made by Ostwald (*Zeitschrift für physikal. Chemie*, 11, p. 501 [1893]), who ascertained the heats of ionisation of the elements, that is, the quantities of heat that become free, or are used, in the passage of gram-atoms of the elements into the ionic state.

A very brief account may be given here of the method by which Ostwald ascertained the value of j (the heat of ionisation) for copper.

When a current passes between copper electrodes through a solution of copper sulphate, copper is dissolved at the anode. The total quantity of heat, w, which is disengaged in this process is 10,200 gram-calories;* this is equal to the algebraic sum of two quantities, namely, the heat of ionisation, j, of copper, and that quantity of heat which is equivalent to the electrical energy, E, corresponding with the difference of potential, π, between the copper electrode and the (normal) solution of copper sulphate. Now as $\pi = +0{\cdot}6$ volt,

* This is determined, indirectly, from the change that occurs in the potential-difference between the copper electrode and a solution of copper sulphate when the temperature changes.

according to measurements (carried out with a capillary electrometer) wherein the potential of the electrolyte = 0, and hence is smaller than the potential of the electrode, the quantity of energy set free, E, when one gram-atom of copper dissolves, is

$$\begin{aligned} E &= 2 \times 96{,}500 \times 0{\cdot}6 \text{ volt-coulombs} \\ &= 27{,}700 \text{ gram-calories.} \end{aligned}$$

Hence, as the equation $w = E + j$ must hold good, it follows that

$$\begin{aligned} j &= 10{,}200 - 27{,}700 \\ &= -17{,}500 \text{ gram-calories.} \end{aligned}$$

This result means that 17,500 gram-calories disappear during the process of ionising one gram-atom of copper; so that the ion of copper is richer in energy, by this amount, than the gram-atom of copper.

It is very easy to deduce the value of j for zinc from the value for copper. The thermo-chemical equation $Zn + CuSO\,Aq = ZnSO_4Aq + Cu + 50{,}100$ calories tells that 50,100 calories are given out when one gram-ion of copper is un-ionised and at the same time one gram-atom of zinc is ionised. Now as 17,500 calories must be set free by the passage of one Cu ion into the non-ionised state, the process of ionising one gram-atom of zinc must produce $50{,}100 - 17{,}500 = 32{,}600$ calories. Hence, one gram-ion of zinc is poorer in energy, by this amount, than one gram-atom of neutral metallic zinc.

If, following Ostwald, each positive electric charge on a kation is represented by a dot (·), and each negative charge on an anion by a dash (′), then ionisation processes may be expressed in thermo-chemical equations as follows :—

$$\begin{aligned} Cu &= Cu^{\cdot\cdot} - 17{,}500 \text{ cals.} \\ Zn &= Zn^{\cdot\cdot} + 32{,}600 \text{ ,,} \\ Cl &= Cl' + 40{,}100 \text{ ,,} \end{aligned}$$

Various other heats of ionisation can be determined in the same way as j was found for zinc, from the heat of ionisation of copper and certain thermo-chemical data. These values are of especial interest. Some of those that have been determined by Ostwald are given here; they are all referred to the quantities of ions which are endowed with a single valency:—

K	= +	61,000 cals.	Pb	= −	500 cals
Al	= +	39,200 „	H	= −	800 „
Zn	= +	16,300 „	Cu	= −	8800 „
Fe	= +	10,000 „	Hg	= −	20,500 „
	(ferro-ion)		Ag	= −	26,200 „
Sn	= +	1000 „			
Cl	= +	40,100 „			

Although these numbers cannot be accepted as quite accurate, because of the difficulties in determining the values of w and E [in the equation $j = w - E$; see p. 64], nevertheless they show that the process of ionising an atom is accompanied sometimes by a gain, and sometimes by a loss, of energy; and that those elements which show greater chemical activity are poorer in energy in the ionic state, whereas energy has to be added from without to the less chemically active elements in order to ionise their atoms. Conversely, the neutralisation of the ions of the former elements can be accomplished only by the expenditure of much energy, whereas the ions of the latter elements readily separate from their solutions. [All the metals which are easily ionised show positive heats of ionisation; the others show negative heats of ionisation.]*

Especial stress should be laid on the fact that the process of ionisation does not necessarily involve a consumption of

* I have intercalated this sentence from Ostwald's paper referred to on p. 63.—[TR.]

[illegible] is that *the energy* [illegible] *during the* [illegible] into electrical [illegible] *system*; *or* [illegible] in the form [illegible] of which forms [illegible] processes of ionisa- [illegible] element when it is [illegible] in accordance [illegible] of the element.

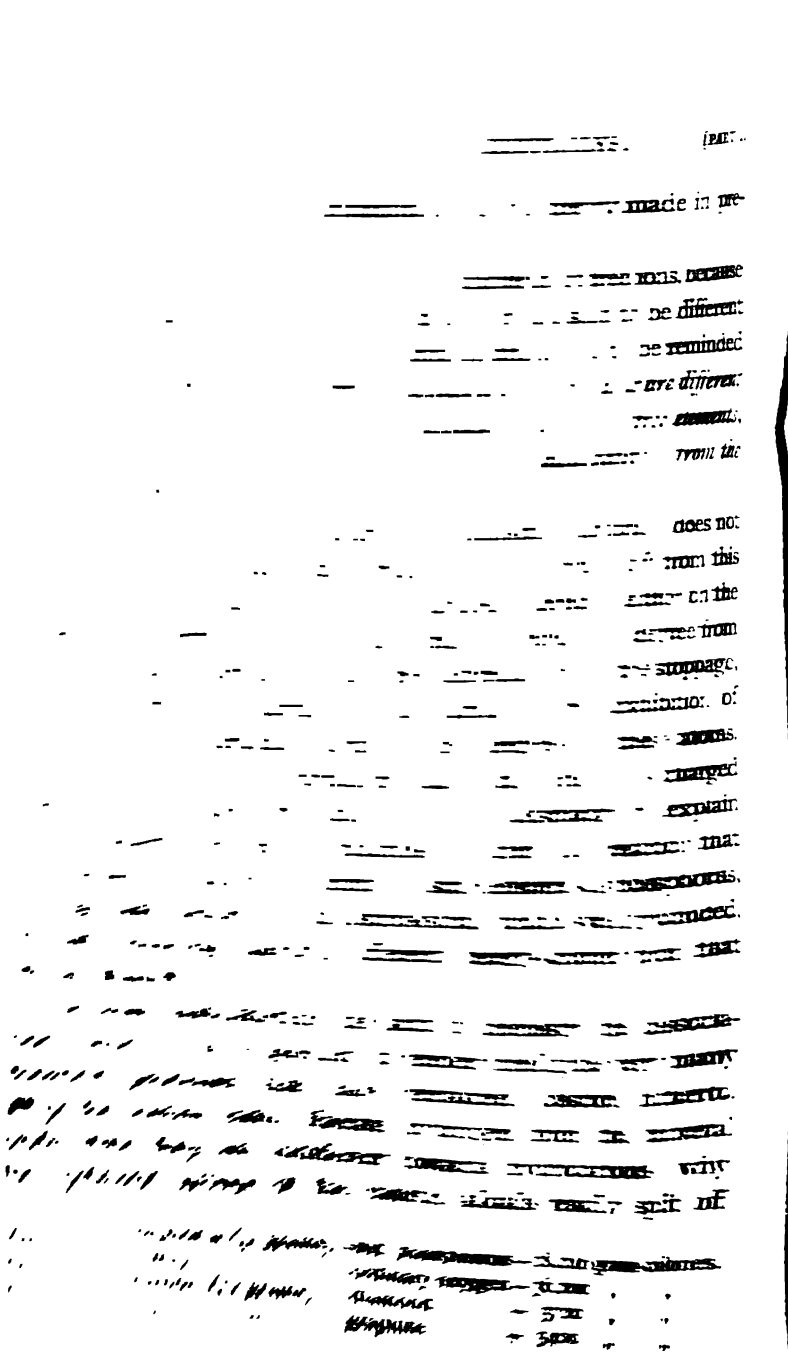
[illegible] of electrolytic [illegible] the number of [illegible] thanks to the [illegible] there are still both physicists and chemists who cannot see their way to accept the existence of free portions of molecules carrying electric charges.

Those physicists, for the most part, regard the way of working of the electrolysing current from the point of view of the older theory of Grotthuss, which dates from the year 1805. This theory represented the work of the current as consisting in the ordering of the molecules in rows, and the separation of the ions, at the electrodes, from this association of molecules; and it was supposed that this explained the use of the electrical energy and its transformation into chemical energy.

[illegible] as 1857 Clausius (*Mechanische Behandlung der Elek-* [illegible] 1879], Part VI.) urged against this view the objection [illegible] the hypothesis were correct, a solution of an electro- [illegible] ild not act [illegible] conductor until the *current-energy* [illegible] ampère) h [illegible] me sufficient to effect the decompo- [illegible] f the mol [illegible] and that from this *moment, which* [illegible] marke [illegible] sudden deviation of a galvanometer [illegible] in the [illegible] ry many molecules must be decom-

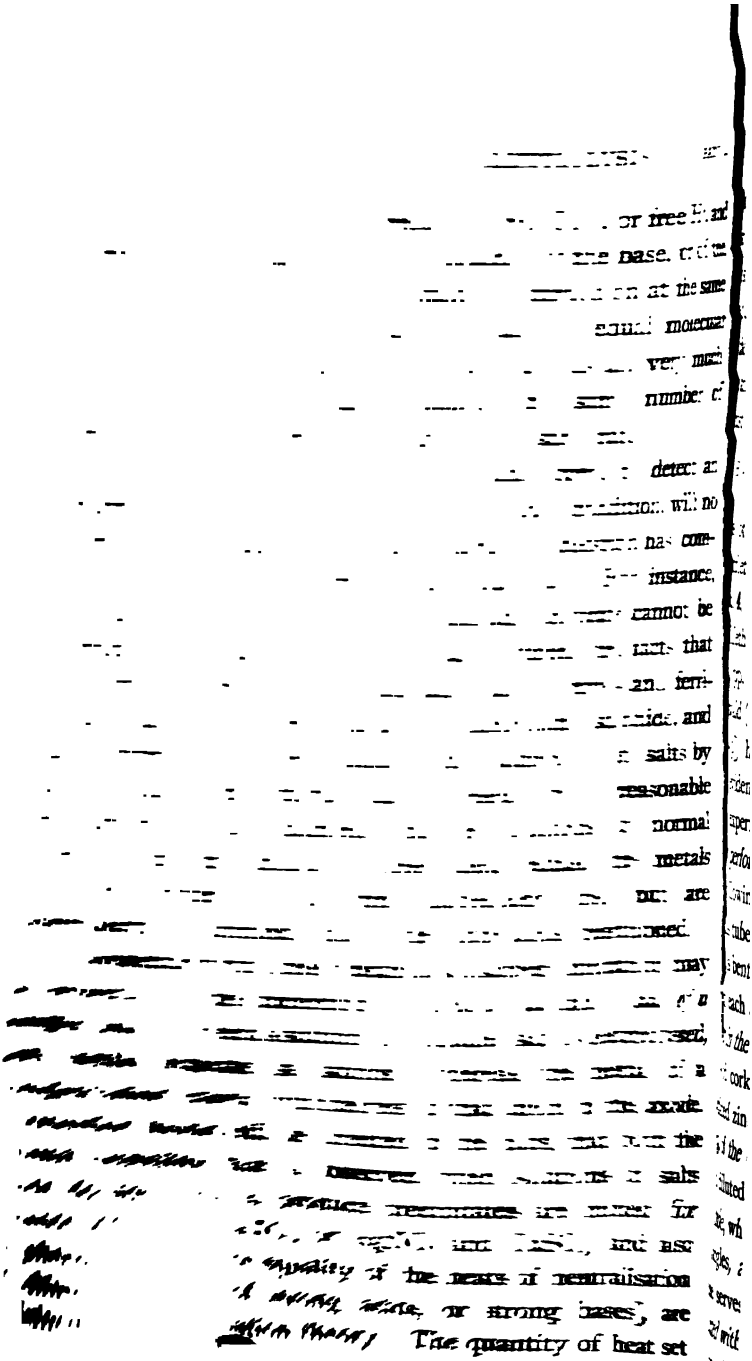
posed all at once. As a matter of fact, a current of the minimum number of ampères is able to accomplish electrolysis, provided the electrodes consist of the same metal as the kation of the electrolyte, and provided the tension that prevails at the electrodes is just sufficient to overcome the electromotive force acting in the opposite direction, which force is generally small, and is dependent both on the material of the electrodes and on the character of the ions, which give up their charges more or less readily. When these conditions are fulfilled, the needle of the galvanometer begins to move. The deviation increases quite gradually as the electromotive force of the current increases, and as, in consequence, the quantity of current passing through the solution increases, the quantities of the ions that are separated also become greater in accordance with the law of Faraday. Experience shows that conductors of the second class obey Ohm's law absolutely; but this could not be the case if the hypothesis of Grotthuss were accepted [without any modifications or additions].

If the energy of the current were really employed in splitting the molecules of the electrolyte, then those electrolytes whose ions are held together by weak affinities, in the chemical sense of that term, are just the electrolytes which ought to exhibit large conductivities. Experience goes against this conclusion also; for a solution of mercuric chloride conducts much worse (because of the smaller dissociation) than a solution of potassium chloride, and when potassium-silver cyanide is electrolysed, the potassium, which must be more firmly held than the silver, goes to the kathode, while the silver travels with the cyanogen to the anode. The dissociation theory is free from those objections which apply to the older theory; it takes the facts of electrolysis into account in a complete way, as has



when the alkalis react with salts of heavy metals, whereas the same groups are not removed from alcohols by similar reactions—for instance, from glycerin, which does not produce a precipitate in copper sulphate solution,—these reactions cannot be understood if it is assumed that the parts of the molecules of the acids and bases mentioned are more firmly held together than the parts of the molecules of the organic compounds. The great readiness to enter into reactions of those inorganic compounds which are electrolytes, the rapidity wherewith they accomplish their interactions compared with the slowness of reactivity shown by the non-electrolytes, to wit the carbon compounds, these facts were made intelligible for the first time by the dissociation theory (*see* Ostwald, *Zeit. für physikal. Chemie*, **2**, p. 270 [1888]). The substances which are the most chemically active in solution are just those substances whose molecules are dissociated; and this is a statement of which not analytical chemistry only, but synthetical chemistry also, especially the chemistry of carbon compounds, makes the most far-reaching applications. Moreover, the final results towards which the chemical processes that occur with the aid of electrolytes tend are at once made manifest by the dissociation theory. For the minute particles exchange ion for ion, and this the more quickly the greater is the mobility of the ions, and the more completely the dissociation has advanced. The dissociation-coefficient of Ostwald, α [see p. 59, where it is proposed to call α the *ionisation-coefficient*], gains a wider meaning as it becomes also the coefficient of activity in chemical reactions, and it will perhaps point the way by which measurements of chemical affinity may be made.

If the saponification of ethereal salts proceeds at the same rate whatever base or acid be used, provided only that th degrees of dissociation of the acids or bases employed are



ree by the neutralisation of a [strong] acid in solution by a [strong] base also in solution to form a salt which remains n solution depends exclusively [according to the theory] on he combination of the H ions of the acid with the OH ions f the base, and it must, therefore, be independent both of he anion of the acid and of the metal of the base; moreover, it must always have the same value,

$$H^{\cdot} + OH' = H_2O + 13{,}700 \text{ cals. at } 20^\circ \text{ [for a monobasic acid]},$$

unless other changes of energy occur in consequence of incomplete dissociation (see Arrhenius, *Zeit. für physik. Chemie*, 4, p. 96 [1889]). [Compare Ostwald's article, "Electrical Methods," in Watts' *Dictionary of Chemistry*, new edition, vol. iv., pp. 189, 190.]

Ostwald (*Zeit. für physik. Chemie*, 2, p. 271, and 3, p. 120 [1888-89]) has described experiments intended to furnish direct evidence of the existence of free ions; but only one of the experiments appears to me to be capable of being readily performed, by the arrangement which is described in the following paragraph.

A glass tube, 40 centims. long and 1 centim. diameter (*RR*, fig. 19), is bent at right angles near the ends, and two pieces of tubing, each about the size of a test-tube, are fused on to it, as shown in the figure. One of these tubes is tightly closed by a good cork, through which passes a rod of very pure amalgamated zinc, *a*. A piece of platinum, *k*, is fused through the walls of the other tube near the bend; the apparatus is filled with diluted sulphuric acid, and a cork is then inserted this tube, which cork carries a narrow tube, bent twice gles, and containing coloured water, *M*. The : serves as a manometer. If the rod of zinc is ted with the positive pole, and the platinum wire egative pole, of a battery of five accumulators,

hydrogen instantly appears on the platinum wire, and the pressure of this hydrogen causes the liquid to rise in the manometer.

Now, if it was necessary for the current first of all to decompose the molecules of sulphuric acid, then the two atoms of

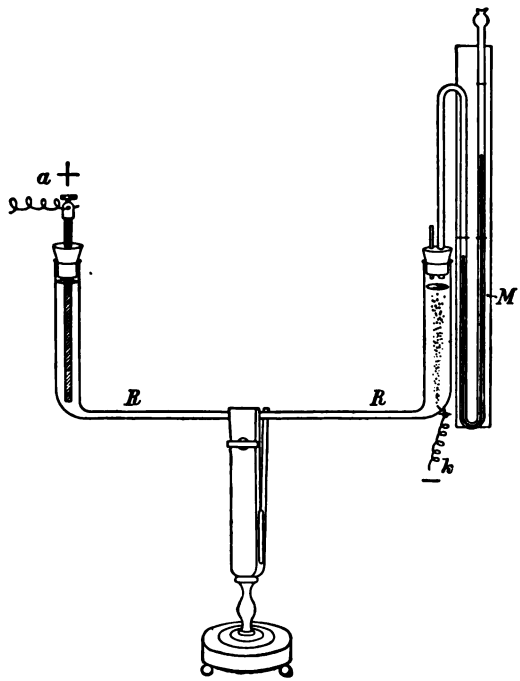


Fig. 19.

hydrogen from which the zinc had withdrawn the SO_4 radicle must have travelled to the platinum through the tube, which is 40 centims. long. Other experiments have shown that this passage of the hydrogen would occupy several hours. But as hydrogen appeared on the platinum at the moment of closing the circuit, free hydrogen ions must have been already present

in the neighbourhood of the platinum, and these must have escaped as gas after their electrical charges had been neutralised.*

The dissociation theory seems, then, not only to be vindicated against all objections, but it is demanded for the explanation of diverse processes. The justness of the theory is exhibited yet more significantly by phenomena which belong to a domain that is somewhat removed from that of electrolysis, and which will be considered in the next part of this book.

* This experiment is explained by supposing the occurrence of a frequent exchange of ions between the molecules of the electrolyte. If such exchanges occur, there must probably be periods whereat the slightest directive force will suffice to precipitate the ions, that are for the moment nearly free, on to the electrodes. (Compare Lodge's *Modern Views of Electricity*, pp. 72-87; and Fitzgerald's "Helmholtz Memorial Lecture" in *Chem. Soc. Journal*, **69**, p. 885 [July 1896].)—[TR.]

PART II.

THE THEORY OF SOLUTIONS OF VAN'T HOFF.

A THEORY of solutions was promulgated by van't Hoff simultaneously with the announcement of Arrhenius' theory of electrolytic dissociation. This theory has achieved extraordinary success in the short time during which it has been known, that is, since the second half of the last decade. The theory has made it possible to bind together, and to establish on a theoretical foundation, a number of phenomena which could not before be brought into line with one another. It has also been of great service in the practical work of chemistry, inasmuch as it has called into existence extremely valuable methods for determining molecular weights.

The points that will be especially attended to in this part are, the connections between van't Hoff's theory and the subject of electrolytic dissociation—for that subject has been greatly aided by the theory—and the elucidation of the conception of osmotic pressure. As the theory of van't Hoff is directly connected with Nernst's theory of the origin of the current, which will be considered in the last part of this book, it is necessary to go somewhat fully into the work of van't Hoff, although it may seem at first sight as if we were dealing with matters that have nothing to do with electrochemistry.

CHAPTER I.

OSMOTIC PRESSURE.

WHEN a body does not react chemically on a liquid wherein it is soluble, we are accustomed to regard the process of dissolution as purely physical and the solution as a molecular mixture. The changes of volume-energy and thermal energy which accompany the process of dissolution are positive or negative according to the state of aggregation of the substance to be dissolved, and these changes generally proceed in the same direction when a concentrated solution is diluted with the solvent. But when the dilution has reached a definite limit, these changes of energy can no longer be observed: the volume of the dissolved substance is then small compared with that of the solvent. The following considerations apply in the main to solutions whose concentrations approach that limit; although more concentrated solutions serve better for certain demonstrations, because they produce more marked effects and produce them more rapidly.

If a more dilute solution of a coloured salt—for instance, an aqueous solution of copper sulphate or potassium bichromate—is poured carefully, with the aid of a cork disc on the end of a glass rod, over a more concentrated solution of the same salt, it is observed that the concentration of the former solution gradually increases, while that of the latter decreases. The molecules of the dissolved substance diffuse from places of greater, to places of less, concentration, until the liquid

homogeneous throughout. The force which produces the diffusion corresponds with the gaseous pressure which compels a volume of gas to occupy a larger space when the chance is given to it to do so. For just as the gaseous pressure drives the gas-molecules to the new limits, so are the molecules of the dissolved body urged to distribute themselves equally in the solvent which has been added.

The following experiment serves to demonstrate the actual existence of such a pressure during the process of diffusion. A cylinder of about 100 c.c. capacity is filled to the brim with a concentrated syrupy solution of sugar, and the cylinder is then covered, air-tight, with a piece of animal membrane. When the cylinder is then sunk upright in a vessel full of water, the membrane begins to swell outwards in a cup-like form, and after some hours it reaches a height of a couple of centimetres. This phenomenon evidently depends on the striving of the sugar molecules to pass into the water outside the cylinder; but as they cannot do this because of the membrane, they stretch the membrane, and water flows into the space that has been formed in the cylindrical cell by this stretching. That the tension of the membrane is very considerable is shown by removing the cylinder from the water and puncturing the membrane with a fine needle; a stream of liquid is forced upwards through the small hole to a height of [illegible] metres.

[illegible] used in this experiment is called *osmose* [illegible] and the force wherewith the molecules [illegible] distance press on the membrane is called [illegible] This pressure is found to be the greater [illegible] is the concentration.

[illegible] exact relations between [illegible] it is necessary to make [illegible] osmotic, that is,

which can be passed through by the molecules of the solven , but not by those of the dissolved, body. This condition is nc : completely fulfilled by an animal membrane ; for the presenc : of sugar can be detected in the water wherein the cylinde : stood for some hours in the experiment that has just bee described.* Perfectly semipermeable membranes are knowr , but they are few in number.

If the epidermal cells from the underside of the mid-rib o a leaf of *Tradescantia discolor* are floated in a 10 per cent. solution of nitre, the protoplasmic contents of the cells may be seen, under the microscope, to become detached from the cell-walls, and to contract, while the salt solution occupies the space between the protoplasm and the walls of the cells. H. de Vries, who studied osmose in plant-cells in 1884, called this phenomenon *plasmolysis*. The delicate pellicle which surrounds the protoplasmic contents of the cells acts as a semipermeable membrane in this experiment. This membrane allows the passage of water from the contents of the cell when the concentration of the salt solution is a very little greater than that of the cell-sap. When de Vries had ascertained the concentrations of those aqueous solutions of different substances which just brought about the plasmolytic condition in plant-cells, he found that these solutions were *equimolecular*, that is to say, he found that they contained quantities of the dissolved substances proportional to the r weights of those substances. *Equimolecular solu- n, exhibit equal osmotic pressures ; they are isotonic* = equally strained). *Hence the magnitude of the*

by boiling a small quantity of the water wherein race of dilute sulphuric acid, and then adding an *solution* (10 grams copper tartrate + 500 grams caustic soda), when a red precipitate of cuprous

osmotic pressure is conditioned only by the number of the molecules in solution.

Valuable although this result is, yet direct measurements of the osmotic pressure of a solution of determinate concentration cannot be made by the plasmolytic method. To effect such measurements an apparatus is required the essential part of which is an artificially prepared semipermeable membrane. The choice of a medium for making such membranes is extremely limited, as very few suitable substances have been discovered, and the membranes made from these substances have possessed the desired property only in respect to the solutions of a small number of substances. But notwithstanding these difficulties, the few investigations of osmotic phenomena that have been conducted with artificial membranes have led to important results, and have incited further speculations.

The earliest experiments were made by Traube (*Archiv für Anat. und Physiol.*, 1867, p. 87). One shall be described here. A mixture was made of 5 c.c. of a 2·8 per cent. solution of copper acetate and 0·5 c.c. of a 10 per cent. solution of barium chloride; a glass tube about 5 mm. diameter was partially filled, by suction, with this mixture, and the upper end of the tube was closed by a piece of caoutchouc tubing and a pinchcock. The tube was then immersed in a 2·4 per
olution of potassium ferrocyanide (equimolecular with
lon of copper acetate), until the levels of the liquids
al. A gelatinous precipitate of copper ferrocyanide
med at the lower end of the tube, and covered the
of the tu · a skin. As this precipitated mem-
ows wat hardly any barium chloride, to pass
it, wat essed into the glass tube, and the
ne was l outwards, like a bubble, by the
pressu by the solution of barium chloride.

Traube supposed that the semipermeability of a membrane of copper ferrocyanide is due to the membrane acting like a sieve, the meshes of which allow the smaller molecules of water to pass, but stop the larger molecules of the dissolved substance. Tamann (*Zeit. für physikal. Chemie*, **10**, p. 255 [1892]) has found, however, that these membranes are quite impermeable by solutions of the chlorides and nitrates of calcium and magnesium, but only partially impermeable by the chloride and nitrate of barium; hence he thinks that Traube's hypothesis is wrong. According to Tamann, freshly precipitated copper ferrocyanide is a hydrated compound which is able to act as a solvent towards certain substances; and the molecules of all those substances which dissolve in this compound are capable of passing through the membrane, while those substances which are insoluble in the compound are held back.

In order to carry out osmotic investigations on a larger scale with the precipitated membrane that has been described, it was still necessary to give to the membrane the proper ability to withstand resistance. This was done by Pfeffer (*Osmotische Untersuchungen*, Leipzig, 1877), by forming the membrane in the walls of a porous clay pot. The preparation of a membrane that is sufficiently compact and cohesive is an operation attended with some difficulty. It succeeds better the smaller the porous pot. Pfeffer used pots 4·6 centims. high and 1·6 centims. diameter. He fastened a glass tube, which served as a stopper, in the neck of a pot wherein a membrane had been formed; and to the side-piece of this
ıbe he affixed a mercury manometer with the free limb
ɔ then completely filled the apparatus with the
ɒe examined, closed it (*see* figure 20), and immersed
rge quantity of water. The mercury gradually rose
ıometer tube, but several weeks elapsed before th

maximum that the tension had been attained, that is, when the closed limb of the manometer was in equilibrium with the osmotic pressure; and in this way [illegible] to measure the osmotic pressure in atmospheres, and so to state the force wherewith the molecules of the dissolved substance pressed on a portion of the surface of the wall of the pot equal in the cross-section of the manometer tube.

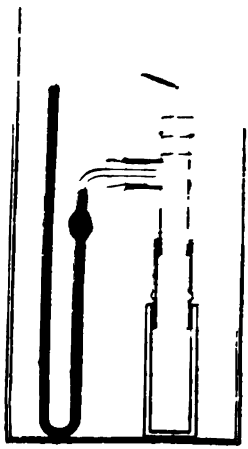


Fig. 20.

Because of their great importance, these experiments have been repeated from time to time with several changes in their arrangement. The most important change has consisted in making the precipitated membrane capable of resisting pressures of several atmospheres. There were reasons for thinking that more perfect semipermeability would thus be attained, and that it would be possible to extend the investigations to a greater number of substances. Reference should be made in this respect especially to the work of Tamann (*Zeit. für physikal. Chemie*, 9, p. 97 [1891]). But, after all, we have not as yet got [illegible] nearer the goal. Good results are to be expected by [illegible]ringsheim's method of forming a very durable [illegible]vanide membrane on a substratum of glycerin. [illegible]sired to examine the phenomena of osmotic [illegible]ely qualita[illegible]v, a bell-shaped glass vessel of [illegible]ay [illegible]oyed (see figure 21); the lower [illegible] is [illegible] centims. diameter, is closed [illegible] by sealing on the bottom of a [illegible] [illegible] size; this porous plate

must be fastened securely by means of sealing-wax. After the glass vessel has stood in boiling water for an hour (that it may be thoroughly saturated with water), it is filled with a 3 per cent. solution of potassium ferrocyanide, and sunk in a vessel which contains a 3 per cent. solution of copper sulphate until the levels of the liquids are equal. If the porous plate fits firmly, the brown precipitate of copper ferrocyanide will not be seen either in the glass vessel or in the liquid outside that vessel. The membrane that is produced acquires a sufficient thickness after three days. The glass vessel is now prepared, once for all, for osmotic experiments; it is filled with a 50 per cent. solution of cane sugar, and closed with a cork through which passes a thermometer tube, *r*, of 1·3 mm. clear thickness, furnished with a scale. A little powdered alkali-blue is shaken into the bore of the thermometer tube before that tube is fixed in its place; this powder adheres to the sides of the tube, and makes the rise of the sugar solution very evident by the blue colour which it imparts to the liquid. If the apparatus is now fastened, by means of the cork *k*, in a vessel filled with water, *C*, the liquid in the thermometer tube rises at the average rate of 1 mm. per minute. After the experiment is finished, even if it proceeds for so long as five hours, the water in *C* shows merely a trace of sugar when tested with Fehling's solution.

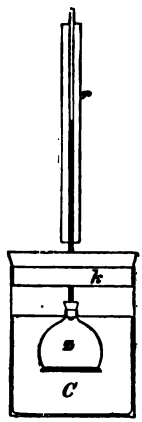


Fig. 21

Results are obtained by the use of a cylindrical cell, the walls of which are made of sufficiently porous unglazed porcelain.* A cell of this kind is got ready for

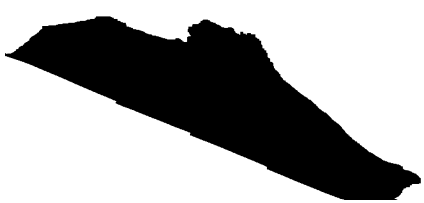
* Obtained at the Royal Porcelain Manufactory, Berlin.

use in the following way. It is thoroughly soaked with water, by repeatedly evacuating under the air-pump [and then immersing in water]. It is then filled with a 3 per cent. solution of potassium ferrocyanide solution, closed with a cork which must not be set more than one centim. into the vessel, and which carries a piece of glass tubing open at both ends, and immersed in a 3 per cent. solution of copper sulphate. After seven days a sufficiently firm membrane of copper ferrocyanide has formed somewhere about the middle of the wall of the cell. For use in a demonstration, the cell is filled with a 50 per cent. solution of cane sugar, and it is then closed by a caoutchouc cork set as far as possible into the cell. The cork carries a ⊢-shaped glass tube, similar to that shown in the apparatus in figure 22; the side-piece of this tube, *T*, is connected, by means of a caoutchouc cork, with the manometer tube, *M*; this tube, which is furnished with a scale and contains [illegible] solution in both limbs, has a bulb [illegible] as shown at *k*, and the longer [illegible] little funnel *t*. The [illegible] with the sugar solution, [illegible] the cork *f*. In order [illegible] quantities that may be [illegible] through *f* and [illegible] flame if a [illegible] the run in a [illegible] the manometer [illegible] flame if the [illegible] by of water

proceeds about four times as quickly as in the preceding experiment.

A Pukall's cell provided with a precipitated membrane seems to be suitable for quantitative, as well as for qualitative, osmotic experiments. When a 1 per cent. sugar solution was placed in the cell, and the manometer was filled with mercury, the mercury rose after some weeks to a height which agreed closely with the pressures found by Pfeffer; and not a trace of sugar could be detected in the water outside the cell.

The following experimental arrangement, recommended by Pfeffer (*loc. cit.*, p. 12), is not suited for measuring pressures, but it has the advantage that experiments can be carried out with it easily and quickly. A glass tube, 12 centims. long and 2·5 centims. wide (*R*, fig. 22), is used in place of a porous pot. The lower edge of this tube, having been flattened somewhat and ground, is brushed over with shellac, and a piece of parchment, *H*, is bound over it very firmly. The precipitated membrane is then formed in this parchment in the usual way. The rest of the arrangement, which is the same as that used in the experiment with a Pukall's cell, has been described above; the glass tube *R* is finally fixed, by means of a cor[illegible] neck of the bottle *F*, which contains [illegible]r. It [illegible]ntioned that 0·1 per cent. of potassium [illegible] the sugar solution, and 0·09 per cent. [illegible]y) of copper nitrate to the water, for [illegible]ing damage done to the precipitated [illegible]nt. The rate at which the [illegible]ies to some extent with the [illegible]mbrane. If the reaction of [illegible]d potassium ferrocyanide is [illegible]ys, a membrane will be pro- [illegible]he liquid in the manometer

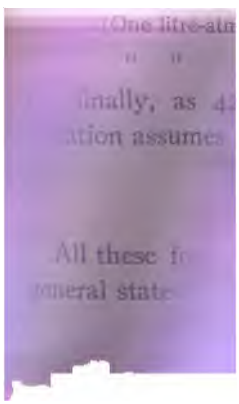


of all gases, measured under the same conditions of temperature and pressure, contain equal numbers of molecules. Not only has this statement been confirmed by numberless determinations of molecular weights, but it has also been deduced directly from thermodynamical principles. One litre of hydrogen measured at 0° and 76 centims. mercury-pressure weighs 0·08956 gram; hence one gram-molecule, that is two grams, of hydrogen occupies 22·38 litres at normal temperature and pressure. In accordance with Avogadro's law, the normal volume, that is to say, the volume occupied by a molecular weight in grams, of any gas must then be 22·38 litres. Now if, following Horstmann, the volume v_0 in the gaseous equation $pv = p_0 v_0 T / 273$ is put as the gram-molecular volume = 22·38 litres = 22,380 c.c., and if it is borne in mind that 76 c.c. of mercury weigh 1033·3 grams, and, moreover, if p is measured in grams and v in c.c., the equation takes the following simpler form :—

$$pv = \frac{1033{\cdot}3 \times 22{,}380 \times T}{273} = 84{,}700\ T \text{ gram-centims.}$$

Or, if p is measured in atmospheres and v in litres, the equation takes this form :—

$$pv = \frac{22{\cdot}38 \times T}{\quad} \quad \text{·0819 } T \text{ litre-atmospheres.}$$



·3 × 100 × 10 gram-centims.
·33 kilo.-decims.)

n-centims. = 1 gram-calorie, the

2 T gram-cals.

for pv are included in the

When the molecular volumes of gases measured in litres are multiplied by the respective pressures and the products are divided by the absolute temperature a constant value is obtained. The equation includes not only Boyle's and Charles's laws, but Avogadro's law also. Very great importance is attached to it in both chemical and thermodynamical calculations.

The following examples will serve to demonstrate the applicability of this gaseous equation.

1. To calculate the volume in litres occupied by 5 grams of hydrogen, the temperature being 27° and the pressure 772·70 millims. of mercury; the volume of 2 grams is

$$v = \frac{.0819 \cdot (273 + 27)}{72{\cdot}70};$$

and it follows that the volume occupied by 5 grams is

$$\frac{.0819 \cdot (273 + 27)}{72{\cdot}70} \times \frac{5}{2} = 64{\cdot}837 \text{ litres.}$$

2. If 80 litres of carbon dioxide at 75 centims. pressure are to be found, the molecular volume at 75 centims. and 30° is determined,

$$v = \frac{.0819 \cdot (273 + 30)}{78{\cdot}76};$$

and the weight that is sought, x, is arrived at by the proportion

$$\frac{v}{44} : \frac{80}{x};$$

hence

$$x = \frac{80 \times 44}{v} = 145{\cdot}5 \text{ grams.}$$

3. How much work is done by 1 kilo. of oxygen in expanding against the atmospheric pressure?

The answer is $1000/32 = 31{\cdot}25$ gram-molecules, which amounts to

$84{,}700 \times 31{\cdot}25 \times 100 = 264{,}687{,}500$ gram-centims.
$= 2646$ kilogram-metres;
$0{\cdot}0819 \times 31{\cdot}25 \times 100 = 256$ litre-atmospheres;
$2 \times 31{\cdot}25 \times 100 = 6187$ gram-calories.

The gaseous equation proved of very signal service to 't Hoff in his further speculations concerning osmotic ssure. An extraordinarily close relation was found between notic pressure, P, and the gaseous pressure, p, when the ation $pv = 0{\cdot}0819\ T$ litre-atmospheres was applied to ffer's results. The osmotic pressure $P = 0{\cdot}649$ atmos. ch a 1 per cent. solution of cane sugar exerts at 0° put by van't Hoff in place of p in the above equation. w as 100 grams of water containing 1 gram of sugar in tion occupy 100·6 c.c., it follows that 1 gram-molecule 342 grams) of sugar is contained in $100{\cdot}6 \times 342$ c.c. = litres of a 1 per cent. solution of sugar. This volume substituted for v in the foregoing equation; and van't f then found $R = 0{\cdot}649 \times 34{\cdot}4 / 273 = 0{\cdot}0818$ litre-atmoeres, which is exactly the same value as that of the gaseous ation.

hen van't Hoff calculated the pressure of a gas whose me is equimolecular with that of a 1 per cent. solution ane sugar—that is, a gas containing 1 gram-molecule in litres—at the temperatures whereat Pfeffer had deterd the osmotic pressures of the sugar solution. The s of the two pressures are given in *Table V.*

TABLE V.

Temperature T.	Gaseous pressure, in atmos. calculated by formula $p = \frac{0{\cdot}0819}{34{\cdot}4} T$	Osmotic pressure, P, in atmos. found by Pfeffer.
273·0	0·650	0·640
279·8	0·667	0·684
286·8	0·683	0·726
288·5	0·687	0·691

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]

[illegible] contains the osmotic pressures P of sugar solutions of different concentrations determined by Pfeffer at 15° ($T = 288$), and beside these are placed the calculated pressures p of gaseous atmospheres of a pressure p. The agreement of the magnitudes p and P in both cases is evident; and a similar agreement is shown for other substances besides cane sugar, as far as measurements of the osmotic pressures of solutions of such substances have gone.

The gaseous equation $p = cRT$, T being atmospheres, is, then, immediately applicable to solutions when the osmotic pressure, P, is put in place of the gaseous pressure, p (in atmospheres), and for the gas-volume, v (in litres), is substituted the volume of the solution, V, that is, the number of litres that contain 1 gram-molecule of the substance. On the ground of this agreement, van't Hoff came to the conclusion that the osmotic pressure is equal to the gaseous pressure which would be observed were the solvent removed and the dissolved substance caused to occupy the same space as the solution [illegible] the same temperature as that of the solution. This [illegible]ion may be stated in the following words: *The mole[illegible] a dissolved substance exert the same pressure again[illegible] semipermeable membrane, during osmotic processes, as [illegible]ld [illegible]inst the walls of an ordinary vessel*

were they in the gaseous state at the same temperature and the same concentration.

While thus extending the law of Avogadro to solutions, on the basis of Pfeffer's researches, van't Hoff also confirmed the law of de Vries, according to which osmotic pressure is not conditioned by the quality of the molecules of the dissolved substance, but only by the number of these molecules; and with these results he associated the conclusion that, under normal conditions, a substance which is not an electrolyte is separated by the process of dissolution into single molecules.

The energetics of solutions must be analogous to those of gases. Hence the same work must be done by the change of the volume-energy of a solution, measured by $P. d V$, as in the case of an equimolecular volume of gas under corresponding conditions of pressure and temperature. The measurement of osmotic pressures by Pfeffer's apparatus depends, on the whole, on this; inasmuch as the air is compressed in the closed limb, and the mercury is raised in the open limb, of the manometer, until the opposite pressure thus produced is equal to the osmotic pressure. In the first case there is merely a shifting of the volume-energy; in the second case there is a transformation of volume-energy into energy of position. A 1 per cent. sugar solution would produce a rise of 6·7 m. in the same solution in the open limb of a manometer. If the cross-section of this limb were 1 sq. centim., then the osmotic work done would be equal to $670 \times 981 \times 670/2 = 219{,}000$ ergs; for 1 c.c. opposes a resistance to the elevation of the liquid equal to 981 dynes, and the mean distance is 670/2 centims. If a lateral overflow-tube were attached to the open limb at a less height than that just mentioned, liquid would flow from this tube until the solution in the cell had become so dilute, by taking up

[illegible] is [illegible] the osmotic
[illegible] it [illegible] pressure if the
[illegible] [illegible] might
[illegible] [illegible] water at
[illegible] [illegible] [illegible] side-tube

[illegible] the water, and consequently, the [illegible] pressure will be [illegible] [illegible] arranging the following arrangement [illegible] [illegible] a vertically placed glass tube, [illegible] [illegible] a thin partition, formed [illegible] [illegible] membrane, which fits securely into the tube, while at the same time is capable of free movement up and down in the tube. Water occupies the space above the partition, and a solution is placed in the space under it. Now, if the pressure of the water-column is greater than the osmotic pressure of the solution, the partition will sink, and the solution will become more concentrated. But if the pressure of the water-column is less than the osmotic pressure of the solution, the partition will rise, and the solution will take up water, and so become more dilute. In both cases the movement of the partition will continue until an osmotic pressure is established which is just compensated [illegible] of the column of water.

[illegible] to do work of a solution, exactly like the [illegible] volume of a gas, is the greater the more [illegible] that is, the more concentrated the [illegible] [illegible] work which the osmotic pressure [illegible] opportunity is afforded the solution [illegible] semipermeable membrane, must [illegible] [illegible] [illegible] degree of con- [illegible] [illegible] is exercised in the [illegible] [illegible] [illegible] directly by

osmotic experiments, because the arrangement of van't Hoff is impracticable in such cases. Measurements can, however, be made indirectly by the aid of the processes of boiling and freezing, which generally make it possible to obtain a more accurate estimation of the osmotic pressure (see Chapters III. and IV. of this part).

As regards the magnitude of osmotic pressure, the high values which this pressure attains even in dilute solutions are certainly surprising. In a 5 per cent. sugar solution at 0° the pressure amounts to $5 \times 0{\cdot}649 = 3{\cdot}2$ atmospheres; and if the osmotic pressure of a half-saturated solution of ammonia is calculated, it is found to be equal to 671 atmospheres at 0°; this number is obtained by the equation $0{\cdot}033\ P = 0{\cdot}0819 \times 273$ (·033 litre of the solution of ammonia contains one gram-molecule, 17 grams, of NH_3). That the vessels wherein such solutions are kept are not shattered is to be accounted for by the internal pressure, calculated in thousands of atmospheres, which holds together the separate particles of the solutions. The osmotic pressure could only gain the mastery, and eventually destroy the walls of the vessels, if these walls were semipermeable and the vessels were immersed in the solvent (see Ostwald, *Lehrbuch der allgemeinen Chemie*, vol. i., p. 673 [1891].

The question as to how osmotic pressure is brought about has been discussed but little. The establishment of a kinetic theory of solutions is a task that is reserved for the future.

The value of the maximum vapour-pressure of a liquid is a measure of the volatility of that liquid. The value for water at 16° is 13·5 mm., while for ether it is 374 mm. at the same temperature.

The depression of the mercury in the barometer tube is found to be smaller when the liquid contains some other substance dissolved in it. The laws which express the lowerings of the vapour-pressures of solutions were elucidated experimentally by Raoult (in Grenoble) in the later years of the last decade (*Zeit. für physikal. Chemie*, **2**, p. 353 [1888]). The work of that investigator was more fruitful than that of his predecessors (Wüllner and Babo), because he began with the more volatile solvents, and he paid especial attention to the solutions of those indifferent substances which did not conduct the electric current, and which themselves exerted vapour-pressures that were extremely small. Working by the barometric method, Raoult arrived at the following statements :—

I. The relative depression of the vapour-pressure

$$\frac{p-p_1}{p}$$

is independent of the temperature, from 0° to 20°. In the formula given p is the vapour-pressure of the solvent alone, and p_1 is the vapour-pressure of the solution.

II. The relative depression of the vapour-pressure increases in proportion to the quantity of dissolved substance, provided the concentration is not made too large.

III. The molecular depression of the vapour-pressure is obtained by referring the relative depression to one gram-molecule of the substance dissolved in 100 grams of the solvent; thus

$$\frac{p-p_1}{p} \cdot \frac{m}{l},$$

quantity of the dissolved substance, in grams,
molecular weight of the substance.

depression of the vapour-pressure has a constant value for different substances in the same solvent, like the osmotic pressure, only on the number of dissolved substance that is present in

the number of molecules of the substance and the
of the solvent are expressed by n and N
calculated by dividing the quantities by weight
solvent by the respective molecular weights),
equation holds good for all solvents:—

$$\frac{p - p'}{p} = \frac{n}{N + n}$$

depression of the vapour-pressure, for any
to the ratio of the number of molecules of the
to the total number of molecules of sub-
present in the solution.

more accurate determinations of vapour-
were made by Raoult, with materials that
carefully, and by the use of the cathe-
the levels of the mercury, and with all
we may illustrate the law of propor-
depression of the vapour-pressure of a
to the quantity of dissolved substance
iment:

equal length, R_1, R_2, R_3 and R_4
millimetre scales, are filled with
in the mercury bath W and
In all the air-bubbles have
mercury must be the same in
flasks of the shape shown
in Hofmann's vapour-density

method) are filled, one with pure ether, another with a solution of 12·2 grams benzoic acid in 100 grams ether, and the third with a solution of 24·4 grams of the same acid in 100 grams ether. The best way of filling the little flasks is to attach them to platinum wire, and to immerse them in the solutions contained in the flasks wherein these solutions have been prepared, and as soon as the little flasks are full, to close them at once with their stoppers. The little flasks are then thoroughly cleaned externally by ether, and they are allowed to rise, stoppered ends downwards, and in the order stated above, to the top of the mercury in the tubes R_2, R_3, and R_4; the fourth tube, R_1, serves to measure the pressure of the air. The levels of the mercury become constant after a time, and it is then seen that if the levels are supposed to be joined by a curve, the curve will be a straight line, as is demanded by the law of proportionality. Although the numbers which are read off on the millimetre scales are only approximately accurate, nevertheless they help towards an understanding of Raoult's law of proportionality. They may, therefore, find a place in *Table VII.* (pp. 96, 97) beside the data of other experiments and the calculations belonging thereto.

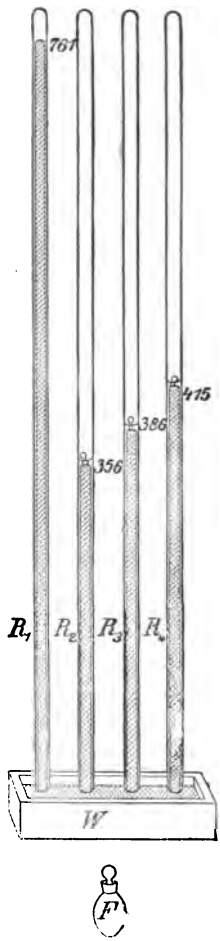


Fig. 23.

The numbers in columns 7 and 8 of *Table VII.* prove, approximately, the second and third laws of Raoult. The numbers in column 9 agree fairly with those in column 7, as

[illegible] Table VII. contains the molecular weights [illegible], salicylic acid, and naphthalene, calculated by [illegible] data given in the other columns.

TABLE VII.

8	9	10	11	12
$\frac{p-p_1}{p} \cdot \frac{m}{l}$	$\frac{n}{N+n}$	$\frac{1}{74\,(78)} \cdot \frac{p-p_1}{p} \cdot \frac{m}{l}$	Molecular weight. Calculated. $m = M \cdot \frac{l}{L} \cdot \frac{p_1}{p-p_1}$	Found by other methods.
0·740	0·0689	0·00999	113	122
·728	·1289	·00984	106	122
·762	·0689	·01030	124	138
773	·1289	·01040	112	138
·762	·0723	·00977	121	128

Inasmuch as both osmotic pressure and relative depression of vapour-pressure are constant for equimolecular solutions in the same solvent, it may be assumed that these two magnitudes are connected causally. As a matter of fact, van't Hoff has deduced the one law from the other by a thermodynamical calculation.

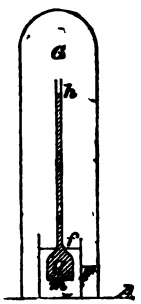


Fig. 24.

In a simpler way, Ostwald (*Lehrbuch der allgemeinen Chemie*, i., p. 728 [1891]), following Arrhenius, has arrived at Raoult's law from the law of osmotic pressure; and his deduction may be repeated here briefly. A small bell-shaped glass vessel, *g* (fig. 24), is closed beneath by a semi-permeable membrane, *m*, and is fitted with an upright tube 1 centim. wide; into the vessel is poured a solution of *n* gram-molecules of some substance dissolved in *N* gram-molecules of solvent, and the vessel is immersed, as far as *f*, in the pure solvent contained in the receptacle *F*. The apparatus is placed on a plate, *A*, and it is covered with a bell-jar, *G*, inside of which a vacuum is produced. The osmotic process causes the liquid to rise in the upright

[illegible] the
[illegible] the
[illegible] small
[illegible] specific
[illegible] equal
[illegible] be

[illegible] is re-

[illegible] pressure
[illegible] pressure
[illegible] vapour
[illegible] Hence,
[illegible] $= Hd$,
[illegible] grams,
[illegible] the form
[illegible] grams; or,

[illegible] the equation

This is the equation found empirically by Raoult; provided that n is very small in reference to N, that is, provided the solution is very dilute.

For limited concentrations H has an extremely high value, and as d varies with H, the pressure π of the column of vapour of the height H cannot be put down, offhand, as $= Hd$. Rather is $\delta\pi = d \,.\, \delta H$; or, as $d = M\pi/RT$, then

$$\frac{RT}{M} \cdot \frac{\delta\pi}{\pi} = \delta H.$$

Integrating this equation between 0 and H, we get

$$H = \frac{RT}{M} \log. \frac{\pi_0}{\pi_H},$$

and in this $\pi_0 = p$ and $\pi_H = p_1$. But it has been found from the osmotic pressure that

$$H = \frac{nRT}{MN}.$$

Hence

$$\frac{RT}{M} \log. \frac{p}{p_1} = \frac{nRT}{MN},$$

or

$$\log. \frac{p}{p_1} = \frac{n}{N}.$$

But

$$\log. \frac{p}{p_1} = \log. \left(1 + \frac{p - p_1}{p_1}\right) = \frac{p - p_1}{p_1} - \frac{1}{2}\left(\frac{p - p_1}{p_1}\right)^2 + \ldots\ldots \frac{p - p_1}{p_1}.$$

Hence it follows that

$$\frac{p - p_1}{p_1} = \frac{n}{N},$$

or

$$\frac{p - p_1}{p_1} = \frac{n}{N + n}.$$

*Thus the empirical formula of Raoult is placed on a theoretical foundation; and the formula $PV = RT$, on which that way of considering the matter rests, is again justified.**

* Compare Poynting, *Phil. Mag.* [5], **42**, p. 289 (October 1896), where formula $\frac{p-p_1}{p_1} = \frac{n}{N}$ is arrived at on the hypothesis of aggregation of molecules of the solvent and the dissolved substance.—[TR.]

in accordance with Raoult's law of vapour-pressure, these two quantities will increase proportionately to the concentration, and that they will have the same value for equimolecular solutions in the same solvent.

As a matter of fact, experiments have led to this conclusion; and it was Raoult who succeeded in solving this problem experimentally, especially by his investigation of organic compounds, and his statement of the results in molecular quantities of these compounds.

Inasmuch as the methods based on determinations of the boiling points and the freezing points of solutions give more accurate estimations of the molecular weights of the dissolved substances, and are more convenient to use, than methods dependent on measurements of vapour-pressures, apparatuses of great delicacy and accuracy have been constructed from time to time for the purpose of determining the boiling points of solutions. Those described by Beckmann are used most commonly (*Zeit. für physik. Chemie.* **2**, p. 639; and **4**, p. 543). The apparatus represented in figure 25 is well adapted for determining the boiling points of aqueous solutions for demonstration-purposes. This apparatus is based on that of Beckmann; certain changes have been introduced, with the object of making the results

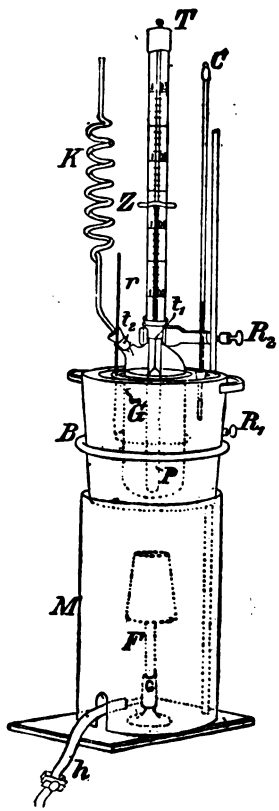
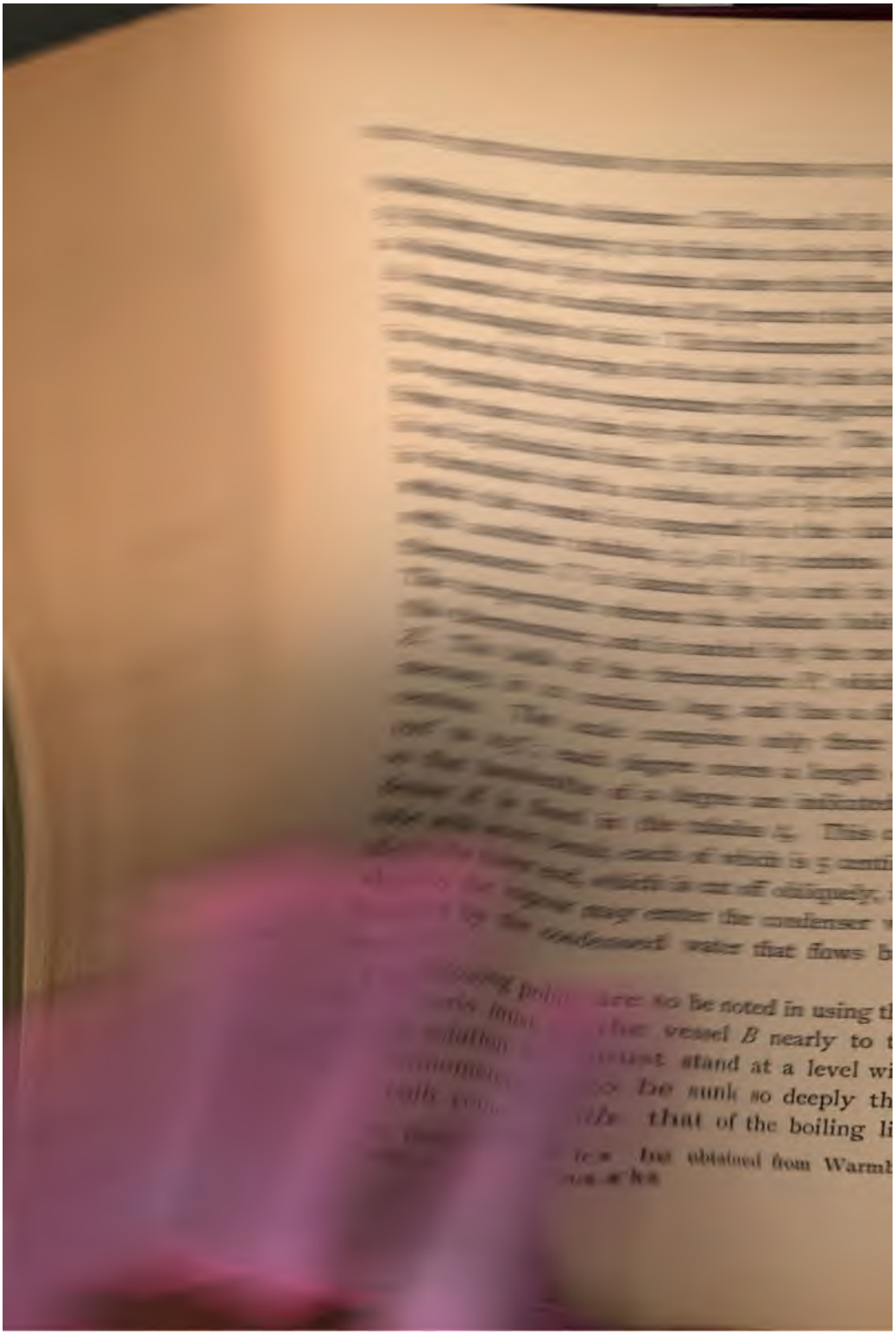


Fig. 25.



better to make the solution and then to transfer it to the apparatus than to add the substance to be dissolved, through the tubulus t_2, to the solvent in the vessel; because only concentrated solutions show sufficiently large increases of boiling point; but the addition of a large quantity of substance to be dissolved considerably increases the volume of the liquid. In order to ensure regular boiling as far as possible, and also to prevent bumping caused by the alternation of overheating and sudden formation of vapour, it is advisable, either to throw little pieces of soapstone into the boiling-vessel, through t_2, just before the temperature of ebullition is reached, or to place a number of little capillary tubes, sealed at their upper ends, in the liquid before the heating is commenced. Moreover, to prevent undue delay in the process of boiling, the temperature of the glycerin should be at most 2° higher than the boiling point of the solution, which may be estimated beforehand within narrow limits. The temperature of the glycerin-bath can be kept constant by regulating the flame by means of the pinchcock h and moving the stirrer r frequently up and down; when the temperature of ebullition is nearly reached, the flame should be not more than from 3 to 4 centims. long. The liquid must be allowed to boil for about ten minutes before the temperature is read, in order that the large quantity of mercury in the thermometer may become heated equally; and the thermometer must be tapped repeatedly because of the inertia of the thread of mercury. Moreover, as the

[illegible] point varies with variation of the barometer, and [illegible]rmometer changes somewhat in course of time, the [illegible]oint of water must always be determined by a [illegible]speriment.

[illegible]*III.* presents the results obtained with an aqueous [illegible]f cane sugar; l shows the grams of sugar in 1[illegible]

[redacted] the

[redacted] tion,

[redacted] ecule

[redacted] If the

[redacted]

[redacted]

[redacted]

[redacted] crease of

[redacted] sugar,

[redacted] is to

[redacted] *saturation*

[redacted] *ruling*

[redacted] *same*

[redacted] determinate

[redacted] weight

[redacted] another sub-

[redacted] be found by

[redacted] contains the

[redacted] values found for

[redacted] closely, and are

[redacted] grams of solvent

[redacted] grams, then

$$= 100.\frac{I}{L(t-t_a)}$$

Troublesome though it is to determine the boiling points of aqueous solutions during a lecture, these boiling points have a very especial interest in connection with electrolysis (see Chapter V.). The experiments with cane sugar which have been described may be turned to further account, as it is possible to invert the cane sugar in accordance with the equation

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$$

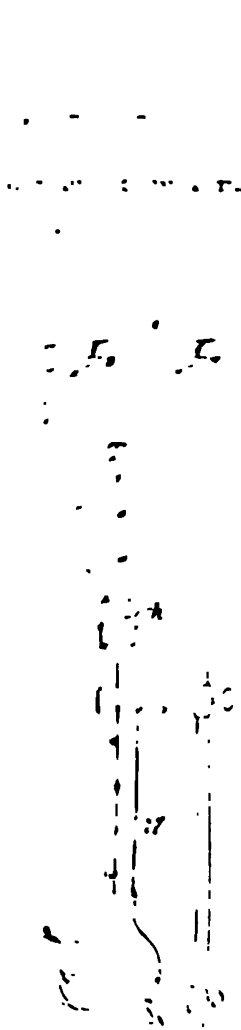
by adding a c.c. of hydrochloric acid containing potassium chloride to the boiling solution, and so to double the number of molecules in solution in less than a minute, and hence to bring about double the increase of the boiling point.

In making determinations of molecular weights by the boiling-point method, care must be taken to select solvents which are without chemical action on the dissolved substance.

The boiling points, and the values of S, of various solvents are as follows :—

	Water.	Alcohol.	Ether.	Acetic acid.	Ethyl acetate.	Chloroform.
t_0 =	100°	78·3°	34·97°	118·1°	72·8°	61·2°
S =	5·2°	11·5°	21·1°	25·3°	26·1°	36·6°.

When one of these liquids other than water is used, thermometers with smaller bulbs may be employed, because of the higher values for S for these liquids. Experiments may therefore be conducted more rapidly with these liquids. The apparatus represented in figure 26, which is of more simple construction than that shown in figure 25, may be employed f[illegible] of demonstration. The bulb of the boiling [illegible] 0 c.c. capacity; its neck is 30 centims. long [illegible] wide. The vessel is placed in a basin made [illegible]ed with asbestos-wool, S, and it must h[illegible]



distance. The scale begins at
and from 30 to 110 it is 30
tims. in length so that each
is represented by nearly
tenths of a degree can be re
Delay in boiling is avoided
way already described (p.
Argand-burner with a
flame, provided with a tall chi
and a regulating stopcock, is re
mended for heating. The b
point of the solvent is deter
first of all, and the substanc
to dissolved is then added thro
the neck of the boiling-vessel
V. contains the result
of the boiling po
in ethylacetat

TABLE IX.

t	$t-t_0$	$\frac{t-t_0}{l}$	$S=\frac{t-t_0}{l}\times m$	$m=26{\cdot}1\times\frac{l}{t-t_0}$
73·5°	0·7°	0·2188	28·00°	119·3
74·1°	1·3°	0·2031	25·99°	128·5
74·7°	1·9°	0·1979	25·33°	125·3

ly fewer precautions are required in determinations ezing points of solutions than in determinations of ing points. Several years ago Ciamician (*Zeit. k. und chem. Unterricht*, **3**, p. 39) described a by which lowerings of freezing points might be d qualitatively by the use of an air-thermometer. he air-thermometer cannot be adjusted readily, the ration-thermometer T (fig. 27) is to be recommended.* strument is useful for many other purposes, such minations of the heats of solution of salts and the heats of metals. The bulb is 14 centims. long, and 5 centim. wide; it is filled with amylic alcohol blue. The scale is 60 centims. long; it extends , from 30° under to 45° above zero. As each degree long, tenths of a degree can be read off with ease. ermometer is placed in the vessel R (wherein the is effected), which has the form of a test-tube. The the solution under examination must be coincident t of the bulb of the thermometer, and must be distant ns. from the rim of the vessel R. The tube R is in the opening of the flask F by means of a disc of The flask F is filled with a concentrated solution of chloride in glycerin or alcohol, and is placed in a

* Stühl, Berlin N., Philippstrasse 22; price 12

ow, because, independently of the defects of the method greater concentrations than are advisable were employed n order to obtain as large differences of temperature as possible.

TABLE X.

1	2	3	4	5	6	7	8	9	10
vent.	Dissolved compound.	l	θ	$\theta_0-\theta$	$\frac{\theta_0-\theta}{l}$	$G=m\times\frac{\theta_0-\theta}{l}$	G according to Raoult.	$m=G\times\frac{l}{\theta_0-\theta}$	m_0
ater	Cane sugar	34·2	−1·8°	1·8°	0·053	18·13°		342·0	
,,	,, ,,	51·3	−2·8°	2·8°	0·054	18·45°	18·5	341·6	342·0
,,	,, ,,	68·4	−3·8°	3·8°	0·055	18·81°		342·0	
nzene	Chloroform	11·9	+0·2°	5·3°	0·444	53·01°		112·7	
,,	,,	23·9	−4·5°	10·0°	0·419	50·01°	51·1	119·5	119·5
,,	,,	35·8	−8·5°	14·4°	0·391	46·72°		128·0	
,,	Naphthalene	12·8	+0·5°	5·0°	0·391	50·05°	50·0	128·0	128·0
,,	,,	25·6	−4·0°	9·5°	0·371	47·19°		134·7	
,,	Aniline	9·3	+0·8°	4·7°	0·505	46·96°	46·3	99·3	93·0
,,	,,	18·6	−3·5°	9·0°	0·484	45·01°		103·3	
,,	Benzoic acid	6·1	+4·2°	1·3°	0·213	25·98°	25·4	234·6	122·0

The analogy between the phenomena of the boiling and the freezing of solutions is shown very well by these results. The freezing point falls proportionally with concentration (column 6), and the depression of the freezing point has the mean value of 18·5° for water, and 49° for benzene, when one gram-molecule of substance is dissolved in the same quantity (100 grams) of either of these solvents (columns 7 and 8). That the depression of the freezing point is dependent only on the number of molecules of substance present in a constant quantity of the solvent may also be illustrated by inverting the 34·2 per cent. solution of cane sugar, and then bringing the solution again into the freezing apparatus, when θ will be found to be $= -3·3°$. The numbers in columns 9 and 10 indicate the importance of determinations of the freezing

points of solutions as means for finding molecular weights. The molecular weights are calculated by the equations :—

$$l : m = \theta_0 - \theta : G$$

or,

$$l : m = (\theta_0 - \theta)\ \mathrm{L}/100 : G,$$

where L expresses the quantity of solvent used in the special experiment.

The results obtained by the boiling-point method and by the freezing-point method show differences from the numbers calculated from the theory; these differences cannot be referred altogether to the errors inherent in the methods. The numbers obtained by the use of Beckmann's apparatus often deviate very markedly from the theoretical values. The values of $(\theta_0 - \theta) / l$ decrease, as a rule, proportionally to concentrations, for solutions in benzene; this is explained by the assumption, which is well founded, that some of the molecules of the substance dissolved in benzene are associated into double molecules. Benzoic acid, especially, forms double molecules when dissolved in benzene. On the other hand the changes both of boiling and freezing points are greater in aqueous solutions of considerable concentration than the theory demands. In these cases the molecules of the dissolved substance must exert an attraction on the molecules of the solvent, which attraction hinders the volatilisation and freezing out of the latter molecules.

CHAPTER IV.

SUMMARY.

THE investigations made regarding dilute solutions have led, so far, to four laws of similar import. These laws are as follows: *Equimolecular solutions of any substances, prepared by using equal weights of the same solvent, exhibit equal osmotic pressures, equal relative depressions of vapour-pressure, equal raisings of boiling point, and equal lowerings of freezing point.* The experimental data allow the inversion of these laws. The magnitudes P, $(p - p_1) / p$, $t - t_0$, and $\theta_0 - \theta$ must, therefore, be proportional to one another for relatively equal concentrations, which are, however, generally small concentrations, and the factor of proportionality can be dependent only on the constants of the solvent. Van't Hoff (see Nernst's *Theoretical Chemistry* [English Ed.], pp. 126, 128) elucidated the relations between osmotic pressure and the three other magnitudes; and he established the following equations, in which M is the molecular weight, and s is the specific gravity, of the solvent, T_0 and T_0' are its absolute boiling point and freezing point respectively, w and w' are the latent heat of evaporation and the latent heat of fusion of the solvent per gram, and K, K', and K'' are collective constants depending on the solvents used.

$$\text{I. } P = \frac{p - p_1}{p_1} \times \frac{819\, s \,.\, T}{M} = \frac{p - p_1}{p_1} \text{ TK atmos.}$$

$$\text{II. } P = (t - t_0) \times \frac{41{\cdot}37 \,.\, s \,.\, w}{T_0} = (t - t_0)\ \text{K}' \text{ atmos.}$$

$$\text{III. } P = (\theta_0 - \theta) \times \frac{41{\cdot}37 \,.\, s \,.\, w'}{T_0'} = (\theta_0 = \theta)\ \text{K}'' \text{ atmos.}$$

terminations can be accomplished much more accurately an measurements of osmotic pressure, satisfy the equation $V = RT$, which corresponds with the gaseous equation; *nce the theory of van't Hoff is confirmed afresh by the ethods of boiling and freezing points.* Moreover, testimony the justness of this theory is borne by the fact that the ıme molecular weights are found for substances in solution om determinations of the boiling and freezing points of the olutions as those which are arrived at by measurements of apour densities.

Another very convincing argument in favour of the theory of solutions has been given by van't Hoff, by his demonstration that the values arrived at for the molecular depressions of freezing points by purely thermodynamical considerations based on the gaseous equation are the same as those that are determined empirically. Let the following reversible process be imagined. A solution of n gram-molecules of a substance in a *very large number*, N, of gram-molecules of a solvent is at the temperature θ_0, and is cooled to θ. In the process of cooling so much heat is withdrawn that N/n gram-molecules of the solvent, that is, the quantity in which one gram-molecule of the substance is dissolved in the original solution, freeze out. Hence $N/n \,.\, M\omega$ gram-calories will be set free, at θ, when ω represents the latent heat of fusion at θ. Let it be supposed that the quantity of the solvent which is frozen is removed from the solution, is heated to θ_0, and is melted at θ_0. In doing this $N/n \,.\, M\omega'$ gram-calories will be taken up, when ω' is the latent heat of fusion of the solvent at θ_0. Now, as latent heats of fusion are smaller at lower temperatures, it is true that

$$\frac{N}{n} M\omega < \frac{N}{n} M\omega'.$$

If ıg solution is brought, meanwhile, to θ_0, th

positive quantity of heat which is added during all these processes is

$$\frac{N}{n} M(\theta - \theta_0) \text{ gram-calories}$$

The solution can perform work at the cost of this heat if opportunity is given by again taking up, osmotically, through a semipermeable membrane, N gram-molecules of the solvent. The initial condition of the cyclical process is thus attained.

This cyclical process can also be performed in the reversed direction. For one can think of N gram-molecules of the solvent being pressed out of the solution through a semipermeable membrane, at θ_0, by a piston, being then allowed to freeze at θ_0, then cooled along with the solution to θ' and being then brought back into the solution wherein it melts. If the whole system were now warmed to θ_0 the cyclical process would be completed, and the quantity of heat

$$\frac{N}{n} M(\theta' - \theta) \text{ gram-calories}$$

would have been in place of the osmotic work that was done on the solution. Moreover, as the formula

$$P' = nT' \text{ gram-calories}$$

shows, P' is the difference between the osmotic pressures of the more concentrated and the more dilute solutions, when a definite volume of solvent which is osmotically taken up, or given out, by the solution—is applicable to the [illegible] which in one case is done on the solution, and in the other is performed by the solution, it follows that

$$\frac{N}{n} M(\theta' - \theta) = P' : T'$$

[illegible] applies only to the first cyclical

ocess; for, in accordance with the second law of the ynamical theory of heat, when heat does work in a reversible yclical process, the portion of this heat which is changed ito work is related to the total quantity of heat added o the system as the fall of temperature is related to the bsolute temperature whereat the heat is taken up by the ystem.

It follows from the foregoing equation that

$$\theta_0 - \theta = \frac{2nT_0'^2}{MN\omega'}.$$

But if one gram-molecule of substance is dissolved in 100 gram-molecules of the solvent, then

$$\theta_0 - \theta = \frac{0{\cdot}02T_0'^2}{\omega'},$$

where T_0' is the absolute freezing point of the solvent, and ω' (which differs but slightly from ω) is the latent heat of fusion of the solvent, calculated for one gram. Now the value found for this quantity $\theta_0 - \theta$ is identical with the empirically determined quantity G. For instance, taking the solvent water, and putting T_0' as 273, and ω' as 79, the value for $\theta_0 - \theta$ is 18·8, while experiment gives $G = 18{\cdot}5$.

A corresponding equation has been deduced by van't Hoff for the molecular raising of boiling point referred to 100 grams of solvent; this formula is

$$t - t_0 = \frac{0{\cdot}02T_0^2}{w},$$

where T_0 is the absolute boiling point, and w is the latent heat of evaporation, of the solvent. This equation satisfies the results of experimental measurements.

Finally, it is to be remarked that the quantities ω and w 'ated from the two equations, using the empiri nd S respectively, and that the values

[illegible]

CHAPTER V.

AQUEOUS SOLUTIONS OF ELECTROLYTES.

ATTENTION has already been drawn to the fact that the investigations which led Raoult to the laws that have been stated in the last chapter, which laws were placed on a theoretical foundation by van't Hoff, were carried out with solutions of indifferent organic compounds in water or in organic solvents. Many substances, namely the salts, acids, and bases, and especially inorganic compounds of these classes, exhibit, when in aqueous solutions, deviations from these laws, and these deviations at first militated against the general recognition of van't Hoff's theory. The values of the quantities P, $(p-p_1)/p$, $t-t_0$, and $\theta_0-\theta$, are higher in these cases than the theory requires. The first and second quantities cannot, however, be measured with sufficient accuracy to enable any kind of regularity in their deviations from the laws to be recognised with certainty. For, on the one hand, membranes of copper ferrocyanide are no longer completely semipermeable at the high pressures that these compounds exert, and, on the other hand, the differences in the vapour pressures of aqueous solutions of the compounds are too small. But further light has been thrown on the matter by investigations into the boiling and freezing points [of solutions of these classes of compounds]. The results of some investigations, made as described in Chapt

, the same

| | | |

reases with increasing dilution, and that the values of i s finally expressible by whole numbers 2, 3, 4 . . .; and, oreover, it has been shown that these values are equal r substances of similar composition; for instance, i is equal 2 for the acids H′A′, the bases B′ (OH′), and the salts ′B′; and i is equal to 3 for the acids H'_2A'', the bases $''(OH')_2$, and the salts A'_2B'' and $A''B'_2$. The same results re obtained whether the values of i are found by the method f osmotic pressure or by that of vapour-pressure, boiling oint, or freezing point. Inasmuch as the quantities $(p-p_1)/p$, $-t_0$, and $\theta_0 - \theta$ are proportional to the values of P, van't Hoff was led to write the general equation in the form

$$PV = iRT.$$

The solutions of all these substances behave as if a greater number of molecules were present than corresponds with the concentrations. The analogy between solutions and gases suggested an explanation of these phenomena by supposing the occurrence of a dissociation of the molecules of the dissolved substances. The anomalous behaviour of certain gases, such as nitrogen peroxide and phosphorus pentachloride, which showed a greater pressure than was demanded by Avogadro's law, had been explained by the hypothesis of dissociation. *Nevertheless, the resolution to employ this expedient in the case of solutions would hardly have been come to had not the substances in question been found to be electrolytes, and had not the theory of electrolysis supported the demand for this explanation.* As a matter of fact, abnormalities in the boiling freezing point phenomena appear only when the ıct the electric current. A solution of sodium er, or of potassium chloride in alcohol, behaves ly as an aqueous solution of sugar or urea; that = 1. But as soon as these salts are dissolv

[illegible] these values
[illegible] the numbers
[illegible] more com-
[illegible] for more minute solutions.
[illegible] values of α, when these are
[illegible] by the help of van't Hoff's
[illegible] equation

ıd on the other hand by the equation $a = \lambda/\lambda_\infty$. (See olumns 9 and 10 of *Tables XIII.* and *XIV.*) With regard to ıe actual signification of the quantities a, it is to be remem-ered that 100 times the value of a represents the number of ıolecules of the substance dissociated out of every 100 nolecules. The number ·89 for sodium chloride, for instance, ells that in the solution under consideration 89 per cent. of he molecules are broken up. *The parts of the molecules of a binary substance must certainly be identical with the ions, and, because of the agreement between the values found for* i *by the two methods already mentioned, the parts of the molecules of all other electrolytes must also be identical with the ions.* The fact, made apparent by the results in *Tables XIII.* and *XIV.*, that the degree of dissociation decreases with concentration, a fact which must follow from the data concerning conductivities, also points in the same direction. Arrhenius has thus explained the peculiar behaviour of aqueous solutions of electrolytes in terms of the law of van't Hoff, although that behaviour seemed at first sight to be opposed to the law; and by doing this he has not only demonstrated the applicability of Avogadro's law to electrolytic solutions, but he has also established the correctness of his own theory of dissociation.

CHAPTER I.

LIQUID CELLS.

IE fact has been known for long that electrical differences : perceived when conductors of the second class are brought o contact. It was not, however, to be supposed that the re contact was the cause of these phenomena.

Nernst explains the occurrence of a difference of potential tween solutions, of different concentrations, of the same ctrolyte, by the different velocities of the ions set in otion by osmotic pressure, whereby the kations become esent in excess in one solution and the anions in the other lution. Inasmuch as the ions bear electric charges with em, an accumulation of positive electricity is brought about one solution and of negative electricity in the other ; and two indifferent electrodes are placed in the solutions and e joined by a wire, a current must be produced in the re because of the equalisation of the two electricities. Cells th[illegible] called *liquid cells*.

nication submitted by H. von Helmholtz to cade[illegible] Sciences in 1889, Nernst calculated of liquid cells on the supposition *ungsber. der Kgl. preuss. Akad. d* cessary to make a brief repetition ions, as they form the basis of the rent. To simplify matters let it

composed of two mon

which are n a

partial press

solution, and let

solution. In ord

coulombs adher

may flow throug

must be move

of the anio

when z (=+v)

solution to th

to the anod

$z+v$) gram-

solution. To these

of the kation from

= one gram-

in the first

of the anion must

of the anion

= one gram-atom. Now,

of a gas in changing

pressure p_1 is

of heat taken

occupies a space of

temperature and under the pressure of 5 atmospheres

the gas as the form of a prism

with, and of centims high. Now let so

pressure amounts to 4 atmospheres. The

vessel but of the vessel occupies the space

atmosphere. The gas performs a certain

amount of work expressed by $\int_{p_1}^{p_2} V\,dp$ must be-
vailable when the volume of a solution, V, which
s 1 gram-atom of kation passes from the osmotic
e p_1 to the lower pressure p_2. Therefore, u / $(u+v)$
atoms of kation accomplish the work

$$\frac{u}{u+v}\int_{p_1}^{p_2} V\,dp,$$

s $pV=RT$, that amount of work is equal to

$$\frac{u}{u+v}\,RT\int_{p_1}^{p_2}\frac{dp}{p},$$

ual to

$$\frac{u}{u+v}\,RT\log.\frac{p_1}{p_2}.$$

the work to be done in raising $v/u+v$ gram-atoms of
n from the pressure p_2 to the pressure p_1 is

$$\frac{v}{u+v}\,RT\log.\frac{p_1}{p_2}.$$

e total work available from the osmotic energy is there-
e

$$\frac{u-v}{u+v}\,RT\log.\frac{p_1}{p_2}.$$

ow if this work is changed entirely into the electrical energy

nount of work during the passage out of the vessel. It raises the air
sting on 800 square centims. to a height of 10 centims.; that is to say, it
erforms an amount of work equal to 1033 . 800 . 10 gram-centims. =
03·8 . 8 kilo-decims. = 8 litre-atmospheres. If the same quantity of
as escapes again, the remaining gas is at the pressure of 3 atmospheres,
he total work is equal to 8 (5 − 3) = 16 litre-atmospheres. Generally,
when 1 gram-molecule of a gas, occupying a space of V litres at
pheres, falls to the pressure of p_2 atmospheres, it
rk expressed by

dp litre-atmospheres.

[illegible] of potential of the

[illegible] absolute

[illegible] absolute units.

[illegible] volt.

[illegible] volt.

[illegible] volt.

[illegible] that a difference of potential may exist between two solutions of different concentrations, not only must u and v be different, but u and v must also differ; and the current flows from the more concentrated to the less concentrated solution when $u > v$, and in the opposite direction when $u < v$. In the case of acids u is always greater than v. A liquid cell formed of a normal solution, and a [illegible] normal solution, of hydrochloric acid, would show a difference of potential, at 17°, equal to

[illegible] . 290 . 3 = ·117 volt.

If the el[illegible] han two ions, the valencies of which [illegible] ation that has been given [illegible] sumes the form

[illegible]

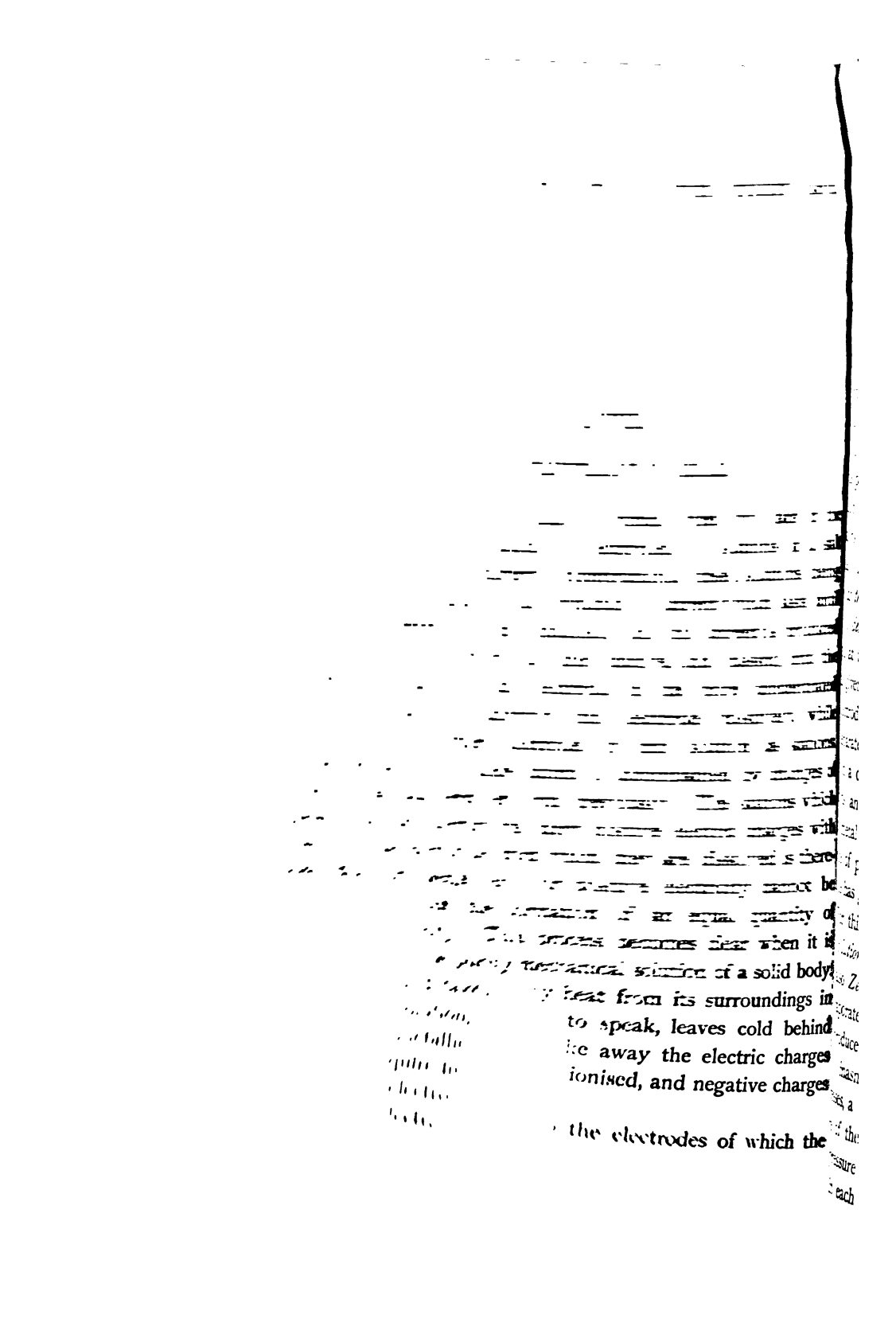
[illegible] two [illegible]-valent

[illegible]

erfectly general formula, which includes the case of two rent electrolytes in contact with one another, has been n by Planck; but that equation need not be considered

he fact is, however, to be emphasised that Nernst has firmed his theory of liquid cells, in a more extended way, experiments. Consequently, in such a cell osmotic energy forms electrical work. Chemical energy does not come o play in this case. One might expect that the current this cell would continue until the osmotic pressures of the o solutions were equalised. But the ions must be con- ıntly giving up their charges to the electrodes. And, as an ectrostatic equilibrium very soon results between the kations ıd the anions, which equilibrium cannot be upset by the ectromotive force of the cell, which is generally very small, ıe current of the cell must very soon cease.

The experimental demonstration of liquid cells may be mitted, because of the small values of the differences of otential of *these* cells.



ent is conducted from without, so in a galvanic cell, the trodes are called the kathode and the anode respectively, rding as the kations or the anions travel to them, and *very case the (positive) current makes its way from the ode through the connecting wire to the anode.* By keeping firmly in the memory, errors in the use of the conceptions ositive and negative poles are easily avoided. The positive : of a galvanic cell is that to which the kations proceed, the positive pole of the source of a current is to be ched to that electrode of a decomposition-cell from which kations must travel with the current towards the other trode. *The positive current always goes in the same ection as the kations, both in the source of the current and in the decomposition-cell.* Inasmuch as the kations are charged at the kathode, the name discharging-electrode is metimes given to the kathode, and the anode is called the tion-electrode when the anions dissolve this electrode.

hree separate differences of potential come under con- ation in a concentration-cell; one is that between the solutions, and the two others appear at the surfaces een the metal and the electrolyte. Nernst has calculated difference of potential between the metal and the elec- te, and he has given an explanation of the origin of this ence purpose he introduced the conception ressure (see contribution already cited . *für physik. Chemie*, 4, p. 129 [1889]). its surface until the pressure of al to the evaporation-pressure evaporation and solution are st dissolve in water until the n is in equilibrium with the salt in question. Similarly ccording to Nernst, a force

[illegible] the normal nature of the metal which [illegible] small ions in the form of ions. This [illegible] must be solution-pressure comes into play [illegible] metal is immersed in an electrolyte and it is the [illegible] have the ions already present in the solution [illegible] is the solution-pressure of a metal and p as the [illegible] pressure of the ions in the solution, three cases [illegible] be distinguished. In the first case P may be greater [illegible] the metal has dissolves like a quantity of salt added [illegible] an indefinite solution of that salt. Kations tend to go [illegible] solution and as positive electric charges are transported [illegible] the kations while an equal quantity of negative electricity remains in the metal. the electrolyte acquires a positive, and the metal a negative potential. However much the value of P may exceed that of p, the number of kations produced by the mere immersion of the metal in the electrolyte can be but small. For the kations collect on the bounding surface between the metal and the electrolyte, by reason of the electrostatic attraction of the kations by the negatively charged metal, and so work against the solution-pressure. Nevertheless, as soon as the free electricities are conducted away through a connecting wire, the solution-pressure manifests itself again, and continues to operate in the way already set forth until p attains the same value as P.

In the second case, when $P = p$, no difference of potential [illegible] p.

[illegible] $P < p$, the metal corresponds with a quantity [illegible] ought into a supersaturated solution of its [illegible] the kations give up their charges to the metal [illegible] ies charged positively, [illegible] acquires a potential. The [illegible] about [illegible] positively charged [illegible] the [illegible] come near it.

The theory of Nernst regards the conception of the ution-pressure of a metal as analogous with that of osmotic ssure. This hypothesis would lead us to expect that the erence of potential, $\mathfrak{p}$, between a metal and the solution one of its salts, at a definite temperature, should be dependent only on the ratio P/p.

The following formula is arrived at by a method similar to at set forth for liquid cells :—

$$\mathfrak{p} = \frac{\cdot 0002}{n} T \log. \frac{P}{p} \text{ volt} \quad \ldots\ldots\ldots\ldots\ldots \text{II.},$$

hen n is the valency of the kation, and $\mathfrak{p}$ is supposed to be the direction from the metal to the solution.

In the case of a concentration-cell of the form

$$M|MS \text{ conc.} \,/\, MS \text{ dil.} \,/\, M,$$

where S represents the anion, the total difference of potential, π, is calculated from the algebraic sum of the three single differences of potential, by means of the equation

$$\pi = \frac{\cdot 0002}{n} T\left[\log. \frac{P}{p_1} + \frac{u-v}{u+v} \log. \frac{p_1}{p_2} - \log. \frac{P}{p_2}\right] \text{volt}$$

$$= \frac{\cdot 0002}{n} \cdot \frac{2v}{u+v} \cdot T \log. \frac{p_1}{p_2} \text{ volt} \quad \ldots\ldots\ldots \text{III.}$$

If the condition which is assumed in calculating π, namely, that the ...lyte is completely dissociated, is not fulfilled, the ...ula runs thus :—

$$\ldots \quad i \quad \frac{v}{u+v} \cdot T \log. \frac{p_1}{p_2} \text{ volt} \quad \ldots\ldots \text{IV.},$$

...ctor. If $u=v$ the equation takes

$$\ldots \log. \frac{p_1}{p_2} \text{ volt} \quad \ldots\ldots\ldots\ldots \text{V.}$$

...nd if $u<v$ then π is greater, than

[illegible] the more concentrated
[illegible] negative electricity flows
wires. For every 108 parts by
[illegible] on K, 108 parts by

eight of silver are dissolved from *A*. The process continues, ith the gradual falling off of the electromotive force of the ell, until the concentrations of the solutions are equalised, nd, consequently, the osmotic energy is completely ex- austed.

The experimental arrangement represented in figure 28 erves to detect the concentration-current by the help of a good galvanometer. The glass tube *R*, which is 15 centims. long

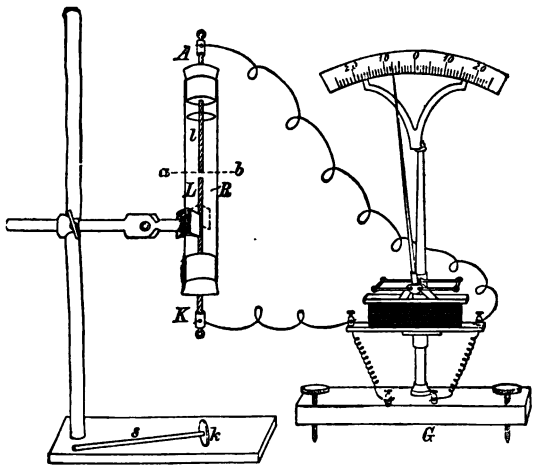
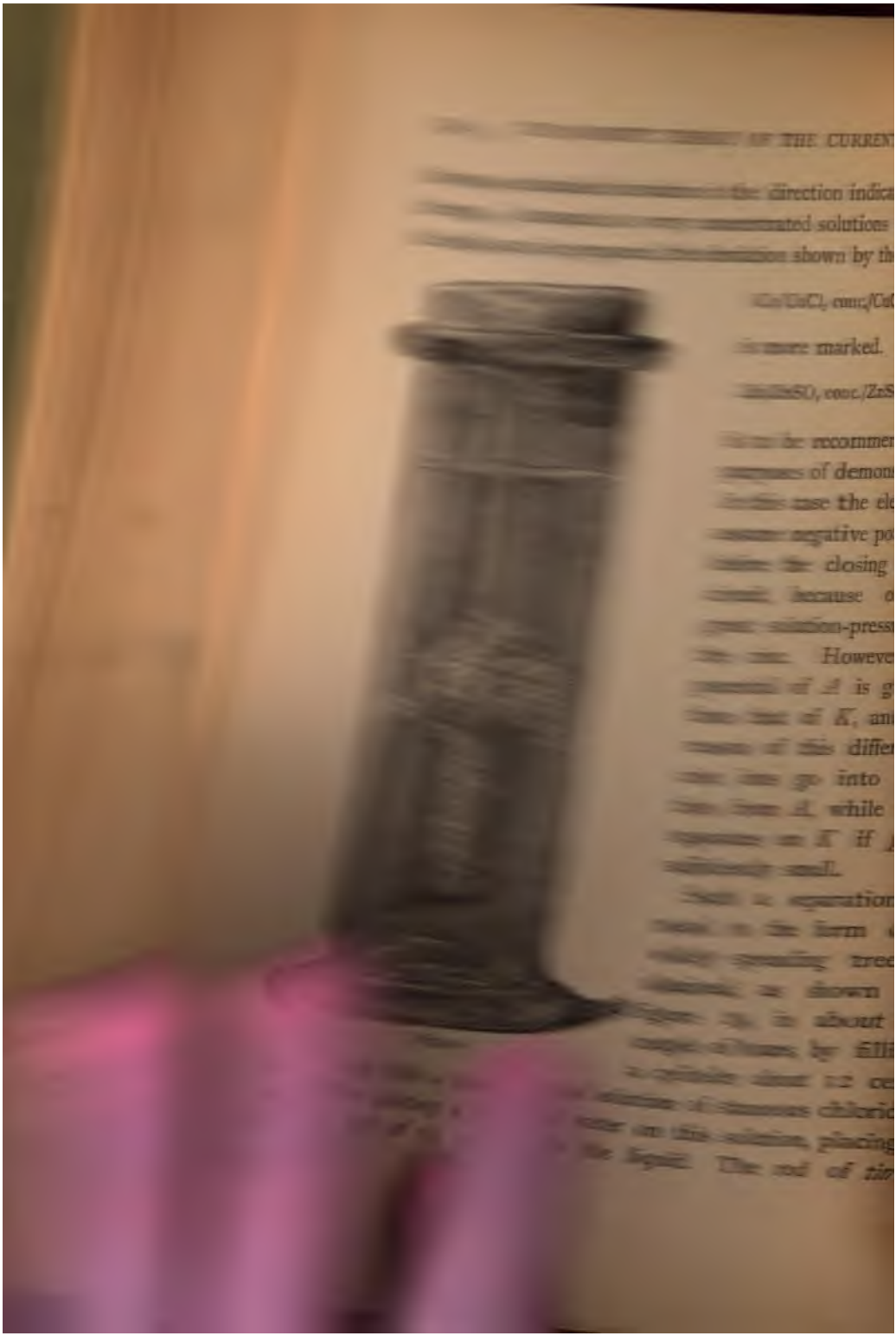


Fig. 28.

and 2·5 centims. diameter, is filled to *a b* with a normal solution of silver nitrate; a layer of water is poured on to the surface of this solution by the use of the glass rod *s*, of which is fastened the cork disc *k*; the s in ed in the liquid, and the lecture- net of which is furnished with a placed in the circuit.* The needle

btained from Keiser and Schmidt, Berlin rks. The instrument that was used in most wherein weak currents had to be detected, id is so delicate that a current of ·00022 ie degree on the scale.



presents both electrodes, and at the same time the connecting wire also. The loss of metal at the upper end of the rod is well shown in the figure.

The effect of the difference of concentration of the solutions is made very evident by the following cell:—In the U-formed tube (fig. 30) are placed the mercury electrodes A and K, which are connected with the conducting wires of platinum wires fused into the glass. The obliquely bent tube which joins the limbs S_1 and S_2 contains a stopper of glass wool. If a cold saturated solution of commercial crystallised mercurous nitrate is poured into the apparatus to the level $m\ n$, the needle of the galvanometer remains at rest, because $p_1 = p_2$. But if a concentrated solution of potassium chloride is now poured, little by little, into the limb S_1, and immediately afterwards the corresponding volume of mercurous nitrate is poured into S_2 for the purpose of restoring equilibrium, the needle shows a deviation, which is greater the greater the quantity of potassium chloride that is added. Mercurous chloride is precipitated in the limb S_1, in accordance with the equation $HgNO_3 + KCl = HgCl + KNO_3$, and the concentration of the mercury ions is hereby decreased. In this way a concentration-cell is produced, wherein it can be easily

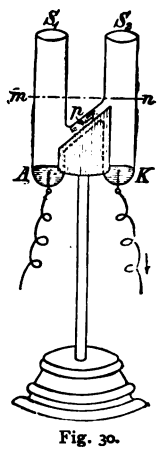
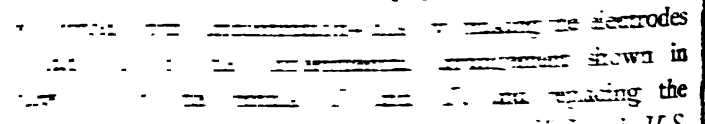


Fig. 30.

[illegible] nce with *Formula IV.*, π increases as p_2 [illegible] minutes the needle returns to the zero [illegible] es covered with the mercurous [illegible] the bottom of the vessel. But [illegible] glass rod, and is thus brought [illegible] at once moves to its former



electrodes shown in ing the and M_1S, difference of namely

$$= \quad -$$
$$= \quad -$$
$$= \quad -$$
$$= \quad -$$

amounts to not more than a few *millionths* this term may be neglected in considering the total is, on the average, much greater; centrations of the two electrolytes ns agree, the more safely may π_2 f π_4 is also very small, as will be is o potentials π_1 and π_3 ulati tting P_1 and P_2 as the nd M_2, p_1 and p_2 as tiv oncentrations of the e the valency of the

metals taken as of equal valency, it follows, in accordance with *Formula II.* (p. 131), that

$$\pi = \frac{\cdot 0002}{n} T \left(\log. \frac{P_1}{p_1} - \log. \frac{P_2}{p_2} \right) \text{volt} \quad \ldots \ldots \quad \text{VI.}$$

$$= \frac{\cdot 0002}{n} T \left(\log. \frac{P_1}{P_2} - \log. \frac{p_1}{p_2} \right) \text{volt} \quad \ldots \ldots \quad \text{VII.}$$

And if the valencies of the metals are different, then

$$\pi = \cdot 0002\, T \left(\frac{1}{n_1} \log. \frac{P_1}{p_1} - \frac{1}{n_2} \log. \frac{P_2}{p_2} \right).$$

The direction of the current within the cell is taken as from M_1 towards M_2.

There are various methods for measuring the electromotive force of the source of a current. When the circuit is open, the measurement is made by a quadrant electrometer, by observing the deviation of the needle, proportional to the electromotive forces, which is brought about on the one hand by the cell to be tested, and on the other hand by a normal element (for instance, a Clark element $Zn/ZnSO_4/Hg_2SO_4/Hg$, for which $\pi = 1{\cdot}438$ volt at 15°). The E.M.F. of a closed cell is read off directly on a sensitive galvanometer, furnished with a high resistance (about 10^5 ohms), and graduated to volts by means of a normal element. Poggendorff's compensation-method is generally used for more accurate electro-

One of the more simple forms in which this is represented diagrammatically in figure 31: ing wire, 1 metre long, of about 50 ohms tant source of current, the E.M.F. of greater than that to be measured; which must be sufficiently large t vary when A is connected with litions the slope of the potential tly definite; when, for instance,

$E = 2$ volts, it amounts to 0·2 volt, and hence to 0·0002 volt per millimetre of the measuring wire. The source of current B and the galvanometer G are connected with the measuring wire so that the currents meet at a. If the sliding contact d is moved until the galvanometer G indicates the absence of current, it is only necessary to multiply the number of millimetres $a\,d$ by 0·0002 to obtain the E.M.F. in volts. (For more details see Ostwald's *Physico-Chemical Measurements* [English Ed.], p. 210.)

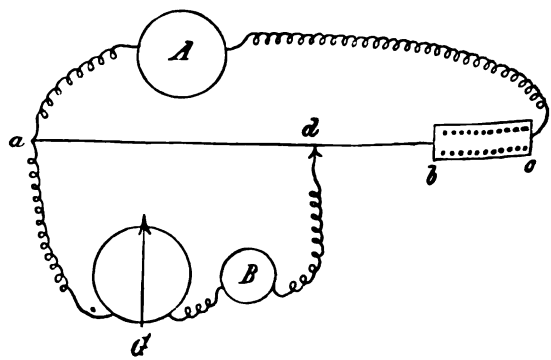


Fig. 31.

Formulæ VI. and *VII.* indicate, what is confirmed by experiment, that π is essentially independent of the nature of the [illegible] π is the same for the cells

$CuSO_4, Cu$

and

CuO_2, CuN_2O_6, Cu

[illegible] by the dissociation [illegible] only when it very [illegible] metallic salt. The [illegible] H_2 is the anode [illegible] hence in dilute

remains positive. This condition is fulfilled as long as the value of P_1 greatly exceeds that of P_2, and p_1 and p_2 do not differ very much from one another.

These conditions are completely fulfilled by the Daniell cell which is now commonly used,

$$Zn/ZnSO_4/CuSO_4/Cu.$$

The E.M.F. of this cell amounts to 1·114 volts at 18°, with equimolecular solutions. This value must remain unchanged, according to the theory, provided the fraction p_1/p_2 maintains the same value, that is to say, provided the concentrations of the solutions are always equal. On the other hand, the E.M.F. must increase if the concentration of the zinc sulphate solution decreases compared with that of the copper sulphate solution. All these conclusions are completely confirmed by experiment, and they are easily understood, for the zinc must go into solution because its solution-pressure considerably exceeds that of the copper, and the passage of the zinc into solution takes place the more easily the fewer the number of zinc ions already present in the electrolyte; moreover, the copper ions must separate from the solution, and this process takes place more readily from a concentrated than from a dilute solution of a salt of copper. The deviations from the normal [illegible]f 1 114 volts are never very large. For even if the [illegible]ti[illegible] of one solution is a thousandfold greater [illegible] o [illegible]ier, the difference amounts only to

[illegible]·0001 log. 1000 = ± 0·087 volt.

A [illegible] interest attaches to the case wherein, ir[illegible] is infinitely small. In that case l[illegible] than $\log. \frac{P_1}{p_1}$. The sign of π is r[illegible] current passes within the cell from

copper to zinc, so that the copper is the anode and the zinc the kathode. These conclusions are realised in practice when the electrolyte around the copper electrode is a solution of potassium cyanide. The electrodes K and A, of zinc and copper respectively, are fixed in the two limbs of an H-shaped tube, as shown in figure 32; the limb S_1 is filled to m with normal zinc sulphate solution (287 : 1000), and the limb S_2 is filled to n with normal potassium cyanide solution (65 : 1000); and a dilute solution of potassium sulphate, which serves as an indifferent conductor, is floated on the top of both solutions to the level op. This cell causes a deviation of about fifteen degrees in the needle of the galvanometer G (fig. 28), in the direction already indicated. On short-circuiting, little bubbles of hydrogen come off from A. After twenty-four hours, a zinc tree has formed from the upper end of K. The changes are somewhat as follows. The copper atoms pass into the solution of potassium cyanide, which is free from $Cu^{\cdot\cdot}$, in the form of ions, and are thus negatively charged. $Cu^{\cdot\cdot}Cy_2''$ is thus produced, while the free $K_2^{\cdot\cdot}$ travel to the SO_4'' anions of the potassium sulphate, and the $K_2^{\cdot\cdot}$ of this salt to the anions SO_4'' of the zinc sulphate, the zinc ions of which give up their charges to the zinc electrode that serves as kathode. The $Cu^{\cdot\cdot}Cy_2''$, however, reacts with $2K^{\cdot}Cy'$, whereby the charges are mutually neutralised, in accordance with the equation

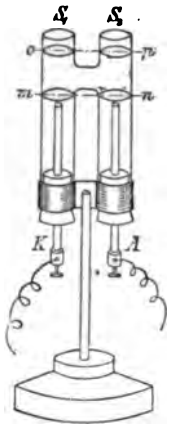


Fig. 32

$$2K^{\cdot}Cy' + Cu^{\cdot\cdot}Cy_2'' = K_2^{\cdot\cdot}(CuCy_4)''.$$

As the copper passes into the complex anion $(CuCy_4)''$, it comes about that the electrolyte around the copper electrode is free from Cu ; hence p_2 remains infinitely small.

Under the circumstances which generally obtain, log. p_1/p_2 maybe put as $=0$ without introducing a serious error. *Formula VII.* (p. 137) then takes this form :

$$\pi = \frac{0{\cdot}0002}{n} T \log. \frac{P_1}{P_2} \text{ volt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{VIII.}$$

Hence, the E.M.F. of a Daniell cell is conditioned essentially only by the ratio of the solution-pressures of the metals; and the main process that occurs in the closed cell is that *atoms of the metal with the greater solution-pressure pass, as ions, into the surrounding electrolyte, while the kations of the second electrolyte discharge themselves on the second metal.* It follows that the first metal, that is, the metal that dissolves and to which the anions of its electrolyte approach, acts as anode, and that the second metal, whereon the kations of the electrolyte thereto appertaining separate in the neutral state, acts as kathode. Inasmuch as the conception formed by Nernst of the electrolytic solution-pressures of the metals must be analogous to that of osmotic pressure, because the experiments that have so far been made verify the calculations that are based on that analogy, it follows that the impelling force of a galvanic cell, by which quantities of electricity are set in motion, must have the character of a pressure-force. In this sense Ostwald rightly speaks of a galvanic cell as a machine which is worked by osmotic pressure (or electrolytic solution-pressure).

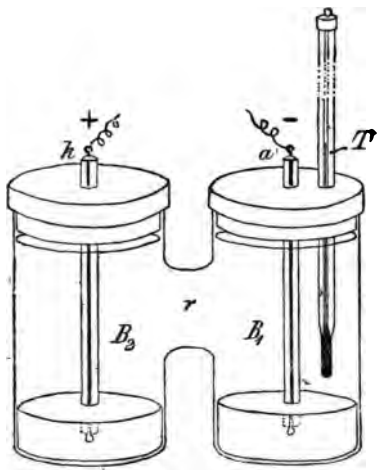
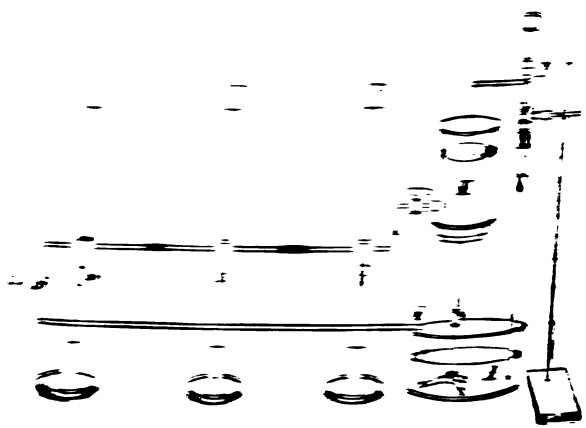


Fig. 33.



cells with
Daniell cells, and lead
which flows away
current depends, on the
apparatus. The smaller the
the smaller will be the quantity
the greater will be the energy
ction against the walls of the
slowly will the pump have to
of chemical change proceeds

in an element which has a thin conducting wire. When the conducting tube has a large cross-section, the pump must work more rapidly in order to replace in K the quantity of water which flows into A; and in the analogous case, a greater quantity of chemical decomposition takes place in the substances which form a galvanic element. The resistance due to friction increases with an increase in the length of the conducting tube, and the quantity of water which flows away decreases. But the connection between the decrease in the quantity of water and the length of the tube is very complicated, whereas the quantity of current is simply inversely proportional to the length of the conducting wire. If liquids other than water are used in the apparatus represented in figure 34, other conditions being unchanged, the quantity of liquid which flows away is found to be dependent on the nature, and especially on the consistency, of the liquids, just as the specific resistances of the various metals are different.

[redacted]

[redacted] zinc goes into solu-

tion. Whereas the chemical energy is transformed into heat when this change is caused to proceed directly by immersing a rod of zinc in a solution of copper sulphate, the chemical energy is transformed into electrical energy when the change takes place in a galvanic cell. Only in this case the process is an indirect one, in so far as it occurs in two phases at the two electrodes with the taking up and the abandonment of electrical charges; thus

$$Zn + Zn''SO_4'' = Zn''SO_4'' + Zn''$$

and

$$Zn'' + Cu''SO_4'' = Zn''SO_4'' + Cu.$$

The process at the anode consists in an oxidation of the zinc by the anion SO_4''. The zinc itself acts as a reducing agent. The electrolyte of the kathode is reduced to copper; it acts, therefore, while the anion SO_4'' is available, as an oxidiser. The copper kathode remains chemically unchanged.

Ostwald drew especial attention to the fact that changes in the charges of the ions generally take place in all chemical processes that occur between electrolytic reducing and oxidising agents, and that these changes are a consequence of the different tendencies of the ions to take up or to give up further quantities of electricity. Moreover, he has proved that such an electromotive process can be brought about if the electrolytes are placed in separate vessels which are connected by an indifferent electrolyte, and electrodes on which these changes of charges can occur are present in the ·· ·olyte. Platinum or carbon is a suitable material f· ·ode s, because these are only required for the ucti·· ·f the electricity, but do not themselves ·th the electrolytes.

l oxidation-cells exhibit the trans-
rgy into electrical energy in a more
·aniell cells, some of these cells may

CHAPTER IV.

REDUCTION-CELLS AND OXIDATION-CELLS.

THE explanations given in the preceding chapter might lead one to suppose that the production of the galvanic current in a Daniell cell is to be ascribed to purely physical forces. Nevertheless, as will be shown more fully in Chapter V., each metal has a special solution-pressure, which is dependent on the nature of the metal, and which must be connected in a very intimate way with the chemical affinity of the metal. Chemical energy is the ultimate source of the electrical energy which is obtained from galvanic cells. In a suitable apparatus —the galvanic cell—chemical energy is transformed into electrical energy. But as the process is essentially dependent on a solution of the metal of the anode, the result of which is the removal of kations from the electrolyte that surrounds the kathode, and as the process is then in the main an expansion of that metal, so the manner in which the chemical energy makes itself apparent in that transformation of energy is of the nature of a pressure-force.

It is certainly true that chemical processes occur in the Daniell cell. In the cell $Zn/ZnSO_4/CuSO_4/Cu$ zinc is changed into zinc sulphate, and copper is precipitated from copper sulphate. The material decomposition is expressed by saying that the zinc separates copper from the copper sulphate, while an equivalent quantity of zinc goes into solu-

tion. Whereas the chemical energy is transformed into heat when this change is caused to proceed directly by immersing a rod of zinc in a solution of copper sulphate, the chemical energy is transformed into electrical energy when the change takes place in a galvanic cell. Only in this case the process is an indirect one, in so far as it occurs in two phases at the two electrodes with the taking up and the abandonment of electrical charges; thus

$$Zn + Zn^{\cdot\cdot}SO_4'' = Zn^{\cdot\cdot}SO_4'' + Zn^{\cdot\cdot}$$

and

$$Zn^{\cdot\cdot} + Cu^{\cdot\cdot}SO_4'' = Zn^{\cdot\cdot}SO_4'' + Cu.$$

The process at the anode consists in an oxidation of the zinc by the anion SO_4''. The zinc itself acts as a reducing agent. The electrolyte of the kathode is reduced to copper; it acts, therefore, while the anion SO_4'' is available, as an oxidiser. The copper kathode remains chemically unchanged.

Ostwald drew especial attention to the fact that changes in the charges of the ions generally take place in all chemical processes that occur between electrolytic reducing and oxidising agents, and that these changes are a consequence of the different tendencies of the ions to take up or to give up further quantities of electricity. Moreover, he has proved that such an electromotive process can be brought about if the electrolytes are placed in separate vessels which are connected by an indifferent electrolyte, and electrodes on which these changes of charges can occur are present in the electrolyte. Platinum or carbon is a suitable material for the electrodes, because these are only required for the metallic conduction of the electricity, but do not themselves enter into any reaction with the electrolytes.

As such reduction- and oxidation-cells exhibit the transformation of chemical energy into electrical energy in a more obvious way than the Daniell cells, some of these cells may

be described briefly here. Figure 35 represents a suitable experimental arrangement. The cells Z_1 and Z_2, of about 100 c.c. capacity, are easily made by cutting off the bottoms of two flasks. The necks of these cells are passed through the corks k_1 and k_2, by which they are fastened into a table-shaped stand; the electrodes K and A pass through the necks, and each is attached to a disc of platinum 3 centims. in diameter. The electrodes are put into connection with a galvanometer. A slightly acidified solution of stannous chloride (112 : 1000), which serves as the reducing agent, is poured into Z_1 till the cell is nearly filled with the liquid (an alkaline solution of stannous chloride acts better); and an acidified normal solution of common salt (58·5 : 1000) is poured into Z_2. The two cells are connected by the syphon H, which is filled with the solution of common salt. The limbs of the syphon are about 3 centims. long; they rest firmly on the nozzle-like expansions of the cells d_1 and d_2, which are barely 1 centim. apart. The needle of the galvanometer remains at rest; but as soon as a few drops of chlorine water (or better, bromine water) are placed on the platinum plate of the electrode K, by means of a pipette, the needle moves rapidly in the direction which indicates that a current is flowing from K through the external circuit to A. The $SnCl_2$ is ready to be changed to the higher state of chlorination, $SnCl_4$. For this purpose two chlorine ions are required, and two positive charges are also needed, to convert the

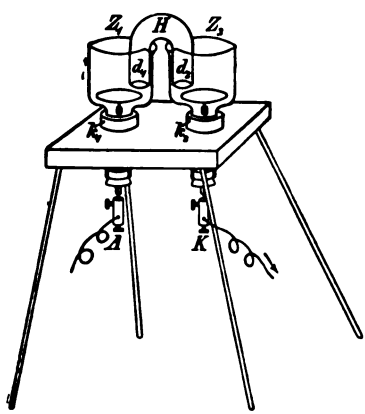


Fig. 35.

divalent $Sn^{\cdot\cdot}$ into the tetravalent $Sn^{\cdot\cdot\,\cdot\cdot}$. Two chlorine ions are produced in Z_2 from one of the chlorine molecules placed therein, and the electrode K becomes positively charged. One $Sn^{\cdot\cdot}$ ion changes to a $Sn^{\cdot\cdot\,\cdot\cdot}$ ion by taking up two positive charges. By this means A is charged negatively. The chlorine ions travel from Z_2 to Z_1. The process continues as long as molecules of chlorine are present on K. The change may be represented by the equation

$$Sn^{\cdot\cdot}Cl_2'' + Cl_2 = Sn^{\cdot\cdot\cdot\cdot}Cl_4''''',$$

which states that the reducer receives two positive charges, and the oxidiser two negative charges. The electrode of the former must, therefore, act as anode, and that of the latter as kathode, and the current must flow from the electrode of the oxidiser to the electrode of the reducer through the wire which closes the circuit. According to Bancroft (*Zeit. für physik. Chemie*, **10**, p. 387 [1892]), such a cell as that described has an E.M.F. of 1·171 volts.

Solutions of gold chloride and mercuric chloride act similarly to chlorine water; they place chlorine ions directly at the disposal of the stannous chloride, while the metallic ions strive to discharge themselves on the kathode. The gold forms a lustrous stain on the kathode. In these cases a solution of sulphur dioxide may be used as the reducing agent, and dilute sulphuric acid as the indifferent electrolyte. The sulphur dioxide is oxidised at the cost of the oxygen of the water, the two hydrogen atoms of which are ionised in order to play the part of kations for the chlorine ions which come from Z_2. The result is that the plate A is again negatively charged. If mercuric chloride is placed on the plate K, a white precipitate of mercurous chloride, which is known to be the first phase in the reduction of mercuric chloride, is very soon seen to be forming under the plate.

The mercurous chloride cannot be produced by some sulphur dioxide which has diffused from Z_1 to Z_2, inasmuch as mercuric chloride is only reduced by a concentrated solution of sulphur dioxide, and not even then until heat is applied.

A more complicated cell, but one which is very instructive, is formed by filling Z_1 with a solution of ferrous sulphate (139 : 1000) to which 10 c.c. of sulphuric acid have been added, and Z_2 with an equimolecular solution of potassium sulphate (87 : 1000 + 10 c.c. H_2SO_4), and touching the platinum disc of the electrode K with a crystal of potassium permanganate attached by sealing-wax to the end of a glass rod. At the moment of touching the plate, the needle moves rapidly. The E.M.F. is 0·968 volt, according to Bancroft. The process is represented by the equation

$$10Fe^{\cdot}SO_4'' + 2H\cdot MnO_4' + 7H_2{}^{\cdot}SO_4'' = 5Fe_2{}^{\cdot\cdot\cdot}(SO_4)_3''' + 2Mn^{\cdot\cdot}SO_4'' + 8H_2O.$$

The O_8 of the two $HMnO_4$, by combining with the H_2 of the $2HMnO_4$ and with the $7H_2$ of the $7H_2SO_4$, forms eight molecules of water. In this way sixteen positive charges become available. Ten of these are conveyed through the connecting wire to the $10Fe^{\cdot\cdot}$, which are thereby changed to ferri-ions, and the remaining six positive charges are used [illegible] $2MnO_4'$, from which two $Mn^{\cdot\cdot}$ are produced, while [illegible]sitive and two negative charges are neutralised.

[illegible]ous cells may be constructed with the help of the [illegible]tus shown in figure 35, wherein electrical energy can [illegible]ined by chemical processes which are related in definite [illegible]s to those already described. In order to make the [illegible]cipitation of silver chloride in accordance with the [illegible]ation

$$NaCl + AgNO_3 = AgCl + NaNO_3$$

[illegible]rical energy, polished silver plates are laid on [illegible]s of the electrodes A and A', the cell Z_1 is

filled with a solution of common salt, and the cell Z_2, and also the syphon H, with an equimolecular solution of sodium nitrate. The galvanometer fails to detect any current from the cells as thus arranged; but the needle moves as soon as a crystal of silver nitrate is placed on the silver plate of the electrode K. The result is due to the passage into solution, in the cell Z_1, of silver ions from the silver plate, and to the separation of crystals of silver on the silver plate in the cell Z_2. Now, as only a small number of silver ions can exist in the solution of common salt, the silver plate in Z_1 is very quickly covered with a film of silver chloride, which darkens in the sunlight. This cell belongs to the class of reduction- and oxidation-cells; but it may also be regarded as a concentration-cell, because the concentrations of the silver ions are very different in Z_1 and Z_2.

According to Ostwald (*Naturw. Rdsch.*, **8**, p. 573), it is possible to transform into electrical energy the chemical energy that is set free in the neutralisation of sulphuric acid and potash. A normal solution of sulphuric acid is placed in the cell Z_2, and a half-normal solution of potassium sulphate in Z_1 and also in the syphon. If a piece of palladium foil, about 4 sq. centims. area, that has been saturated, electrolytically, with hydrogen, is now laid on the platinum plate of the electrode A, and a stick of caustic potash is kept in contact with this palladium foil for a short time, little bubbles of hydrogen rise from the platinum plate of the electrode K, and the needle of the galvanometer indicates a powerful current flowing from K. The prepared palladium foil acts in this case like solid hydrogen. It is known that palladium foil has the property of occluding such large quantities of hydrogen that the hydrogen burns visibly when the foil is heated for a short time in a Bunsen burner. The hydrogen occluded by palladium, like the metals, possesses

a certain striving towards ionisation, and while it becomes ionised the electrode A is negatively charged. The $H^{\cdot}$ ions thus produced meet with the OH' ions of the potash and combine with them to form neutral water, while the $K^{\cdot}$ ions travel to Z_2, where they compel the $H^{\cdot}$ ions of the sulphuric acid to become un-ionised at the electrode K. The processes amount to the formation of water, as is also always the case in the formation of salts by the reactions of acids and bases; thus

$$2KOH + H_2SO_4 = K_2SO_4 + H_2O.$$

The peculiarity of the process in this cell is that the hydrogen which is required by the hydroxyl ions of the base for the formation of water is presented to them in the form of occluded hydrogen which must first be ionised at the anode. An extraordinary profusion of hydrogen is not required, inasmuch as the quantity of hydrogen which is used in Z_1 is obtained again in Z_2.

Ostwald classes the gas-cells, about the theory of which there has been much dispute, among reduction- and oxidation-cells, and by so doing he gives a very simple explanation of the production of the current in these cells. The hydrogen-chlorine cell is the most active. The cell Z (fig. 36), which has a capacity of about 200 c.c., is furnished with three tubuluses, t_1, t_2, and t_3. The middle tubulus must be narrow, in order that there may be but a small distance between the two side tubuluses. The tubes R_1 and R_2, which are 20 centims. long and 1 centim. wide, are placed in the tubuluses t_1 and t_2. The conducting wires from the pieces of platinised platinum foil *

* To platinise platinum, that is, to cover it with finely divided platinum, it is made the kathode in a decomposition-cell containing a dilute solution of platinic chloride mixed with a considerable quantity of hydrochloric acid; another piece of platinum foil is used as anode. An accumulator may be used as the source of the current.

and K are fused through the upper ends of R_1 and R_2. ne whole apparatus is filled with dilute sulphuric acid. lectrolytic hydrogen is then allowed to accumulate in R_1 to .e level a, by connecting A, as kathode, and a piece of atinum foil pushed through t_3, as anode, with the source of current. The tube R_2 is then filled to b with chlorine. hen the connecting wire from K is joined to that from A, powerful current of 1·42 volts is obtained. A single gas-ement of this kind suffices to work a sensitive alarm-clock.

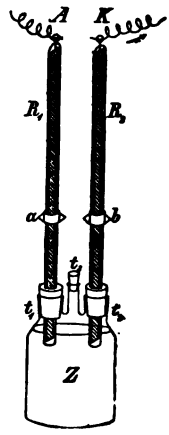


Fig. 36.

According to Ostwald, only those elec-odes are suitable for gas-cells which are ble to occlude gases. For it is only hen it is occluded that a gas is in a con-tion to manifest its electrolytic solution-ressure, and this is especially the case ith hydrogen. The current is produced n the hydrogen-chlorine cell exactly as he current is produced in the stannous loride-chlorine cell which has been de-ribed already. Chlorine ions are readily med in R_2 ($Cl_2 = 2Cl' + 80{,}200$ cals.), and this means K becomes charged positively. ese ions attract hydrogen ions from R_1, so t the occluded hydrogen in R_1 is obliged to form new s. Hence the electrode A becomes charged negatively. hile the current passes through the cell, equal volumes of drogen and chlorine disappear, as is required by Faraday's w. When the cell is short-circuited, the liquid rises in the bes R_1 and R_2 about 3 centims. in an hour.

A hydrogen-oxygen cell shows the smaller E.M.F. of 08 volts. The explanation of the origin of the current in is cell is somewhat more complicated. Each oxygen atom on the kathode side combines with two $H^{\cdot}$ ions, after these

and the
two atoms of
solution as
fresh quan-
ıf gas in
from the
that the
n the pro-

to work an
ıdicator than
ıediate a
minutes t_3
l. In
give the
ıf the gas-
practical

following
Five
rectangular
ıating with
platinum
mm.
wires are
which
ıies cut
ıf the parallel-
ınside of the
ıgement is im-
ıme sulphuric
end a of that
are attached is

connected by the commutator U (key at e) with the positive pole of a battery of two accumulators, B; and the end c of the copper bar which is attached to the five platinum plates is connected, directly, with the negative pole of the battery. The charging current produces a marked evolution of gas in the gas-battery. After charging for five minutes, the current from the gas-battery shows, at first, an E.M.F. of 1·5 volts; and after fifty minutes, and when a resistance of 1127 ohms is intercalated, the E.M.F. is still 0·7 volt. This shows that the apparatus has a relatively large capacity, which is due to the large quantity of gas that is occluded by the platinum plates. The discharging current is sufficiently powerful to

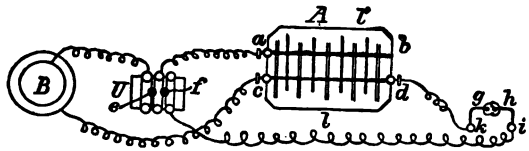


Fig. 37.

melt a thin wire of platinum 10 mm. long. This effect may be shown very well by fastening two isolated copper wires vertically on a small board, 10 mm. apart, connecting the upper ends of these wires, g and h, by a piece of thin platinum wire, surrounding the platinum with a little fresh gun-cotton, and connecting the lower ends of the copper wires i and k with d and U; if the key is put into f, after the gas-battery has been charged for one or two minutes, the gun-cotton takes fire.

In the year 1865 J. Thomsen had constructed a gas-battery of 50 cells (*Pogg. Ann.*, **124**, p. 498), each with two platinum plates, one cell of which was charged momentarily by the current from a Grove element, by an arrangement of a circular board that rotated 20 to 25 times per minute, while

CHAPTER V.

THE SOLUTION-PRESSURES OF THE METALS.

ACCORDING to Nernst's theory of current-production the E.M.F. of a Daniell cell with equimolecular electrolytes is expressed by *Formula VIII.* (p. 141); if this theory is to be tested by direct trials, it is necessary to find values for the solution-pressures, P, of the metals, by experiment. There is no great difficulty in arranging the metals in a series in the order of their solution-pressures. It it only needful to determine whether one metal is able to precipitate another from the solution of one of its salts, and hence, because of a greater solution-pressure, to draw away the electrical charges to the kations of the second metal. The following is the order for some of the well-known metals: zinc, cadmium, iron, lead, copper, mercury, silver. But it has not yet been found practicable to determine the values of P quantitatively.

Nevertheless, it is possible to calculate these values by the aid of the following equation, which expresses the difference of potential $\mathfrak{p}$ between a metal and the solution of one of its salts:—

$$\mathfrak{p} = \frac{\cdot 0002}{n} T \log. \frac{P}{p}.$$

The values of n, T, and p are given directly; and since an electrode has been found, in recent years, which shows no

... with the electrolyte, ... way of an empirical ... at least in principle. ... whereby this could ... demonstrating the be- ... slowly from a ... sulphuric acid. ... will serve to ... The glass ... one metre long ... filled with mercury. ... with a funnel, *T*, a ... fused into ... thermometer tubing, ... about $\frac{1}{3}$ mm. ... dilute sulphuric ... about one ... with which a ... by means of a ... the glass. ... the stream ... from the capillary ... one ... and although both ... of the same metal, ... in the galvanometer ... which passes through ... the battery.

According to the theory of Helmholtz which is supported by the experiments of Lippmann, the current is accounted for by the relations between the electric potentials and the surface-tension of the mercury. The cell $Hg\,|\,H_2SO_4\,|\,Hg$ produces no ... itself for the mercury electrodes show

equal positive potentials against the sulphuric acid which soon becomes saturated with mercurous sulphate. But when the mercury of the flowing electrode assumes the form of drops, it draws away a positive charge from the liquid, and gives this charge up again to the mercury in the beaker at the moment when the drops coalesce with this mercury.

Paschen (*Wied. Annalen*, **41**, p. 42 [1890]) has arranged the dropping electrode in such a way that the difference of potential between it and the electrolyte is practically equal to zero. By immersing the metal in the electrolyte, and joining it and the dropping electrode with an electrometer, the difference of potential between the metal and the electrolyte can be measured.

The difference of potential that has been most accurately determined, up to the present, is that between mercury and mercurous sulphate. The determination gave

$$\underset{\longrightarrow}{Hg/Hg_2SO_4} = -0{\cdot}99 \text{ volt.}$$

From this value, and from the value of 1·514 volts found by Wright and Thompson for the E.M.F. of the cell $Zn/ZnSO_4/Hg_2SO_4/Hg$ at 18°, the following potential difference is deduced:—

$$\underset{\longrightarrow}{Zn/ZnSO_4} = 1{\cdot}514 - 0{\cdot}99 = +0{\cdot}524 \text{ volt.}$$

This value is somewhat too large, as the zinc sulphate solution is only dissociated to 80 per cent. The value must be diminished by

$$^1/_2 \,.\, {\cdot}0002 \,.\, 291. \log. {}^{100}/_{80} = {\cdot}003 \text{ volt,}$$

so that the corrected value $\mathfrak{p}$ is

$$\underset{\longrightarrow}{Zn/ZnSO_4} = +0{\cdot}521 \text{ volt.}$$

presents the calculated and corrected differences of tential, p, between the metals and normal solutions of their lts.

TABLE XV.

A.	B.	C.	D.
$\overrightarrow{Zn/ZnSO_4/MgSO_4/Mg}$	− ·725 volt	Wright and Thompson	$\overrightarrow{Mg/MgSO_4}$ = + 1·243 volt
Zn/ZnSO$_4$/CdSO$_4$/Cd	+ ·360 ,,	F. Braun	Cd/CdSO$_4$ = + 0·158 ,,
Zn/ZnSO$_4$/FeSO$_4$/Fe	+ ·440 ,,	F. Braun	Fe/FeSO$_4$ = + 0·078 ,,
Zn/ZnSO$_4$/Pb(C$_2$H$_3$O$_2$)$_2$/Pb	+ ·607 ,,	Wright and Thompson	Pb/Pb(C$_2$H$_3$O$_2$)$_2$ = − 0·089 ,,
Zn/ZnSO$_4$/CuSO$_4$/Cu	+ 1·100 ,,	F. Braun	Cu/CuSO$_4$ = − 0·582 ,,
Zn/ZnSO$_4$/Ag$_2$SO$_4$/Ag$_2$	+ 1·539 ,,	Wright and Thompson	Ag$_2$/Ag$_2$SO$_4$ = − 1·024 ,,

The numbers in column D are characteristic magnitudes for the metals, provided that the temperature is taken as 18° and normal solutions of the salts are employed. The nature of the anion is generally unimportant, as this need be considered only when it greatly decreases the solubility of the salt. These values may indeed be liable to errors of a few hundredths of a volt, as they are all based on a single measurement, namely, that of the difference of potential between mercury and mercurous sulphate. But the discovery of methods of measurements which shall lead to more accurate determinations of the values of p is only a matter of time. The equation for p indicates that the sign of these values is determined by the relation of the values of P and p; hence, as $p = 22{\cdot}3$ atmos. for normal solutions, the sign is dependent only on P.

The values of P can be calculated from the equatic referred to. The results are presented in *Table XVI.*

TABLE XVI.

1	2	3	4
Metal.	Valency.	Solution-pressure, P, in atmospheres.	Weight, in grams, of metal in 1 litre of solution of the sulphate.
Mg	2	$0{\cdot}115 \cdot 10^{14}$	$1{\cdot}238 \cdot 10^{13}$
Zn	2	$1{\cdot}786 \cdot 10^{19}$	$0{\cdot}520 \cdot 10^{20}$
Cd	2	$0{\cdot}599 \cdot 10^{7}$	$3{\cdot}166 \cdot 10^{7}$
Fe	2	$1{\cdot}068 \cdot 10^{4}$	$2{\cdot}676 \cdot 10^{4}$
Pb	2	$1{\cdot}950 \cdot 10^{-2}$	$1{\cdot}805 \cdot 10^{-1}$
Cu	2	$2{\cdot}228 \cdot 10^{-19}$	$0{\cdot}313 \cdot 10^{-20}$
Hg	1	$2{\cdot}178 \cdot 10^{-16}$	$0{\cdot}390 \cdot 10^{-16}$
Ag	1	$0{\cdot}567 \cdot 10^{-18}$	$0{\cdot}547 \cdot 10^{-19}$

The values of the solution-pressures of the metals, with the exception of that of lead, are sometimes very great and sometimes very small; and, at the first glance, these values are difficult to understand. But when it is realised that the theory of Nernst represents the solution-pressure of a metal as the striving of the metal to overcome the opposing osmotic pressure of the kations which are already in solution, in order that the atoms of the metal may become ionised, then it is seen that the numbers in the third column express those osmotic pressures which the kations of the electrolyte must first possess in order that the ionisation may be impossible, and that the value of $\mathfrak{p}$ may be equal to zero. Now this would be the case if the quantities of the metals expressed, in grams, in column 4, and calculated by means of the formula $\mathfrak{p} V = R T$, were contained in one litre of the solutions of the sulphates. But these quantities are either very large or very small, with the exception of that for lead, so that the gram-atomic weights of the metals (for mercury and silver the double atomic weights) present in one litre of the normal sulphate solutions either very much exceed, or very much fall short of, these quantities.

It follows, therefore, that the values of $\mathfrak{p}$ must always be positive for the metals magnesium, zinc, cadmium, and iron, and always negative for the metals copper, mercury, and silver, even although the concentrations of the electrolytes vary within the possible limits. This will be intelligible if the character of an osmotic pressure is ascribed to the solution-pressures of the metals, and the theory of electrolytic dissociation is accepted, according to which the energy consumed in separating the molecule of the electrolyte into its ions does not enter into the consideration of the question. It will be understood that the electrolyte in which zinc is immersed assumes a positive potential, and the metal itself a negative potential, because the tendency of the zinc to convey positively charged ions to the electrolyte asserts itself. The reverse of this must, however, occur with copper, for the osmotic pressure of the copper ions of the electrolyte overcomes the solution-pressure of the copper. Hence the state of affairs is such that kations give up their positive charges to the copper, and the electrolyte maintains a negative potential. Now if the cell $Zn/ZnSO_4/CuSO_4/Cu$ is closed, both the solution-pressure of the zinc and the osmotic pressure of the copper ions become permanently effective, and the result of this is that the electric current flows through the connecting wire from copper to zinc, from the kathode to the anode.

If the values of $\mathfrak{p}$ in *Table XV.* are correct, then the experimentally determined E.M.F. of a cell, π, composed of any pair of metals in that series and equimolecular solutions of their salts, must be equal to the difference of the calculated values of $\mathfrak{p}$ for these metals. Experiment confirms this conclusion. For instance, Streintz found for the cell $Cd/CdSO_4/CuSO_4/Cu$

$$\pi = 0{\cdot}743 \text{ volt};$$

a [illegible]

[illegible]

The observed value [illegible] Hg_2SO_4, Ag is

[illegible]

as the calculated value [illegible]

[illegible]

A difference between the E.M.F.s of these two cells can be demonstrated experimentally by means of a galvanometer, making the corresponding metals and using equimolecular solutions of the electrolytes. Two rods of cadmium and magnesium, 3 mm. thick, are used as the anodes, in small test-tubes (7 × 2 centims.). Two bent plates of copper and silver, 6 centims. high and 2 centims. wide, serve as cathodes. The electrolytes contain 56 grams cadmium sulphate, 63 grams copper sulphate, 60 grams magnesium sulphate, and 117·5 grams sodium chloride per litre of water. The galvanometer is adjusted to a resistance of 300 ohms. The cadmium-copper combination produces a deviation of 7, and the magnesium-silver combination of 15, degrees.

The following conclusion may be drawn from this agreement between theory and practice, in accord with the theory of Helmholtz: *The E.M.F. of a cell has its origin, essentially, in the contact between the metals and their electrolytes come into contact with each other.*

If two different Daniell cells, which are so arranged that the cathode of the one and the anodes of the other consist of the same metal, are disposed one behind the other, it may be assumed that the total E.M.F. of the combination would be equal to the E.M.F. of a cell containing the anode of one of the combination as anode and the kathode of the

ther as kathode. The calculated value of π for the combination f cells $Zn/ZnSO_4/CdSO_4/Cd$ and $Cd/CdSO_4/CuSO_4/Cu$ is

$$\pi = (\cdot 521 - \cdot 158) + (\cdot 158 + \cdot 582) = 1\cdot 103 \text{ volts};$$

nd, as a matter of fact, the same value is found for the cell $Zn/ZnSO_4/CuSO_4/Cu$ (law of the electromotive series).

The foregoing discussion leads us to regard a list of metals arranged in order of the values of p as the true electromotive series of these metals. Such a series is essentially chemical in its character, as the solution-pressure is a chemical constant of each metal. (If the metals are arranged in conformity with their readiness to undergo oxidation, the order is the same.) The following electromotive series results from Neumann's estimations of the values of P :—

Mg, Al, Zn, Cd, Fe, Co, Ni, Pb, H, Sn, Cu, Hg, Ag, Pd, Pt, Au.

The electromotive series which were drawn up formerly should be referred to the differences of potential between the metals themselves, as these were supposed to be determined by a condenser in the air; and the opinion was held that the E.M.F. of galvanic cells was to be traced almost wholly to these differences of potential. But the fact was overlooked that the isolation of the isolating layer of the condenser could not be perfect, inasmuch as the moisture, and also the salt, in the air act as electrolytes in the experimental measurements. As a matter of fact Edlund's investigations of the Peltier's effect showed that the differences of potential arrived at by comparing the metals one with another are of small magnitude which have but slight influence on the E.M.F. of galvanic cells. The following simple experiment shows that direct contact of metals has very little effect in developing electromotive force, and that the origin of this force is much rather to

be assigned to the action between metals and electrolytes. Copper wires are soldered to a nickel and a silver coin, and these wires are laid on a galvanometer; when the coins are thoroughly cleaned and then pressed one on the other, the needle remains at rest. But if a disc of blotting paper is brought between the coins, a deviation—a very small one it is true—of the needle occurs. If a drop of a solution of common salt is placed on the paper, the needle suddenly moves through about twelve divisions; after about a minute the needle certainly siwngs back to the zero point, but this is due to polarisation (see Chapter VI.).

It is therefore imperatively necessary to pay no regard to the older electromotive series; and this the more, because the production of electrical energy by the mere contact of two substances is altogether against the law of the conservation of energy. Moreover, the old contact theory gave no explanation of the part played by the electrolyte in the production of the current, nor did it indicate the significance of the chemical processes that occur in the cell.

As regards hydrogen, it is to be remarked that the general behaviour of that element shows that it must be looked on as a metal, especially as large quantities of it can be taken up by certain metals, particularly by palladium,* and the products of these actions behave like alloys. Now, if a small plate of palladium is saturated, electrolytically, with hydrogen, and is then immersed in a solution of copper sulphate, the plate is very soon covered with a lustrous layer of copper. In a similar way, gold, platinum, silver, and mercury, are precipitated; but lead, iron, cadmium, zinc, and magnesium, are not precipitated.

* Palladium is capable of occluding 936 times its own volume of hydrogen.

ıng facts are in accordance with these observa-
of the lead, iron, etc., class dissolve in acids with
hydrogen, whereas metals of the class which
d, platinum, etc., do not evolve hydrogen from
›oking such secondary reactions as those which
nitric acid). Hence the value of the solution-
hydrogen occluded by palladium must lie between
he solution-pressures of copper and lead. Ex-
with a palladium-hydrogen plate and a norma
tion, at 17°, showed a difference of potential
— ·23 volt, putting the potential of the plate as zero;
e solution-pressure of the hydrogen is calculated
414 . 10^{-3} atmospheres.

to be expected that future researches in electro-
ry will much extend the list of the values of p.
labours, which are reserved for the future, will not
ontribute to the more exact extension of the new
›-chemical theory, but, as Ostwald insists, they will
›e productive of fruit in the field of pure chemistry,
› far as they will make determinations of chemical
ty possible.

ıe more accurate knowledge of the electromotive series
ıetals in electrolytes has also very great practical interest.
ıerever structures made of different metals, whether alloys,
combinations of different metals in contact, or metals
ıich are encrusted with other metals mechanically or
ılvanoplastically, are exposed to the influence of bodies
recipitated from the atmosphere, there is a state of affairs
uitable for the formation of short-circuited cells. In such
ases one metal acts as the dissolving electrode and the other
as the electrode which leads away the current. The former
is therefore most exposed to destruction, while the latter is
protected to a certain extent. An iron wire which has bee-

normal acid solution is used, the iron acts as the electrode which conducts the current away, even when the cell is short-circuited for twenty-four hours, and tin can be detected in the solution by mercuric chloride. The change of pole is most marked in a half-normal solution of ammonium nitrate (40 : 1000), for after one minute the needle of the galvanometer moves in the opposite direction. In this case the iron acts for a moment as the kathode, and immediately afterwards as the anode. If the electrodes are dried carefully, the same phenomenon is repeated when they are again immersed in the liquid. But the iron remains as the kathode if the salt solution is considerably more dilute or more concentrated. A solution of sodium chloride produces similar results; the solution must be from normal to three times normal (58·5 to 175·5 grams per litre) if the polarity of the iron is to be reversed.

It is evident from these experiments that iron and tin come very near one another in the electromotive series. The other conditions which influence the polarity of a single cell composed of these two metals may be left undecided; it is certain that the concentrations of the electrolytes have a marked effect.

The well-known fact, that tinned iron is more liable to rust when exposed to the atmosphere than ordinary iron, is generally attributed to the occurrence of galvanic processes. If this supposition is correct, it follows that the substances precipitated from the atmosphere must act as electrolytes towards the combination of iron and tin in such a way that the iron becomes the dissolving electrode. Salts of iron must be formed, and then decomposed with the production of rust.

The following experiments may serve to confirm this view. The apparatus represented in figure 39 (p. 172) is filled with 124 c.c. of distilled water. When rods of iron and tin

CHAPTER VI.

INTENSITY OF FIXATION, AND POLARISATION.

E results arrived at in the last chapter become of especial portance in that they afford information regarding the nimum electromotive force required for the electrolytic composition of a substance, and they also advance the comehension of the phenomena of polarisation, regarding the eory of which there has been much uncertainty. When a rrent, whether it be such a current as is produced in a mple galvanic cell or one which flows through an electrolytic ll, causes changes in the electrolyte or on the electrodes, the rrent is always weakened; it is customary to refer this fact polarisation.

Figure 39 represents an electrolytic cell filled with a normal olution of copper sulphate wherein two rods of copper, *A* nd *K*, are immersed as electrodes. There is a difference of otential of ·582 volt on both electrodes, as copper ions strive o separate on both. A galvanic element may be constructed with a similar apparatus, by using a dilute solution of sulphuric acid (1 : 20) and electrodes of zinc and iron. The E.M.F. of this cell is small; but by introducing a resistance of about 1000 ohms, it is further reduced. The rod of copper *A* (fig. 39) is now connected with the iron-pole, and the rod *K* with the zinc-pole, and a galvanometer is placed in the circuit. Notwithstanding the minimum difference of potenti

at A and K, the current flows through the decomposition-cell, and the deviation of the needle remains constant for a long time. But the positive potential on A increases; in consequence of this, copper ions travel from A to K. The SO_4 ions cause the copper of A to send new copper ions into the electrolyte, and this in proportion to the abandonment of their charges by copper ions at K, where the positive potential is decreased by the current that is led into the cell. Hence the concentration of the electrolyte remains constant, and the electrodes do not suffer change. The only result of the current is to transport copper from A to K.* That a very small difference of potential suffices to do this depends on the fact that the energy which is required to form ions at the electrode A (17,500 cals. for one gram-atom of copper) is produced by the process of un-ionising at the electrode K.

Fig. 39.

An exactly similar result is produced if the copper rods A and K are replaced by rods of zinc, and a solution of zinc sulphate is used in place of the solution of copper sulphate; only the deviation of the needle is somewhat less, and, on account of the positive heat of ionisation of zinc (32,600 cals. for one gram-atom of zinc), energy is set free at A and used at K.

In neither case does the galvanometer indicate the existence of a polarisation-current when the electrolysing current is stopped, but the needle returns to the zero point. The electrodes show themselves to be *incapable of polarisation.*

* If the current that is led into the cell were stronger and continued for a longer time, a difference of concentration would soon be brought about at the electrodes, the consequence of which would be the production of a concentration-current in the direction opposite to that of the primary current.

This phenomenon is always noticeable when a primary current does not bring about any changes of composition in the decomposition-cell, and hence when the direction in which the current passes is of no importance. The same conditions obtain in the Daniell cell, and, hence, the E.M.F. of that cell is constant, provided that considerable changes in the concentration of the electrolyte do not occur in consequence of the cell being kept in use for too long a time.

But the result is different when the electrodes are insoluble, and, therefore, the anode is incapable of conveying ions into the electrolyte. Let A and K (fig. 39) be platinum electrodes, and let the electrolyte be a normal solution of sulphuric acid. If the poles of a powerful current-producer, say an accumulator-cell, are connected with these electrodes, a permanent decomposition is brought about. The deviation of the needle remains almost constant. The hydrogen ions travel to K and are set free there. The SO_4 ions betake themselves to A, and, could these ions exist in the free state, they would be un-ionised there. As a matter of fact oxygen is given off at A, in the proportion of one gram-atom of oxygen for every two gram-atoms of hydrogen produced at the kathode. The formation of oxygen is due to the neutralisation of two OH ions of the water (which is dissociated to a very small extent), in place of one SO_4 ion, as shown by the equation

$$2OH' = H_2O + O.$$

As the OH ions disappear more water is dissociated, so that the processes repeat themselves. The gases that are given off at the electrodes are partially occluded by the platinum; and when the decomposition-cell is short-circuited, these gases strive to pass again into the ionised state. In this way state of affairs becomes that which obtains in a gas-cell,

the galvanometer indicates a polarisation-current flowing in the direction opposite to that of the primary current. The E.M.F. of the polarisation-current is not affected by the nature, or the concentration, of the oxyacid used, as these factors do not influence the occlusion of the gases.

If the weak zinc-iron cell is used to produce the primary current for the decomposition-cell $Pt/H_2SO_4/Pt$, the needle of the galvanometer shows only a slight deviation and very soon returns to the zero point. This deviation, lasting for a short time only, is due, in all probability, to the abandonment of their charges at K by a few hydrogen ions, inasmuch as the solution-pressure of hydrogen is much smaller than the osmotic pressure of the hydrogen ions that are present. But the further passage of the current is checked, because the primary current is too weak to neutralise OH ions at A, and, hence, the SO_4 ions attract the hydrogen ions from K towards A, so that the discharging of these ions is no longer possible. Still the primary current maintains a certain difference of potential at the electrodes, while the decomposition-cell behaves like a condenser. If the cell is short-circuited, a polarisation-current arises while the charges of the electrodes equalise one another, and this current causes a deviation of the needle in the opposite direction lasting for a short time.

In investigating polarisation it is very convenient, according to Friedrich C. G. Müller (*Zeit. für d. physik. und chem. Unterr.*, **8**, 1895), to bring about the reversal of the current by means of a Morse-key. The experimental arrangement will be understood from figure 40. If the primary current is taken from a single dry element, E_1, and the cell Z is composed of $Pt/H_2SO_4/Pt$, the needle of the galvanometer G_1, which indicates the direction of the primary current, very soon swings back to the zero point, and G_2 marks a polarisation-

current, which lasts for a short time, in the opposite direction. The column of liquid in the manometer M does not rise, as evolution of gas does not occur. The formation of gas becomes apparent in the manometer (which is provided with a three-way cock) only when a second dry element, E_2, is intercalated, and the deviation of the needle of G_1 is then constant.

It has been observed that the primary current begins to

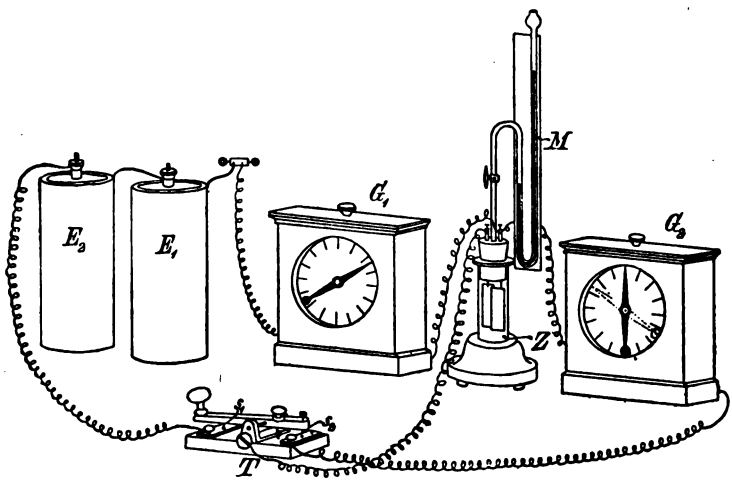


Fig. 40.

force its way permanently through the dilute sulphuric acid when the tension at A and K attains an average value of 1·6 volts.* In accordance with this it is to be supposed that a

* The statements about this value differ much. There are especial factors which influence this gas-polarisation: for instance, the solubilities of the gases in water, and their occlusion by the electrodes; the size, the character of the surfaces, and the distances apart, of the electrodes; the quantity of air in the electrolyte, etc. These factors have a material influence on the pressure to which the products of decomposition exposed; and the E.M.F. of the polarisation-current increas increasing pressure (see *Gas batteries* in Chapter IV.).

...ges
...ar
...ce of
... the
...on is
...al, in
...enced
...erature.
...um, and
...e intensity
...gen, copper,
...e charges
...e of electrical
...auses electrical

...understand that electro-
...e electric charges of

ergy to become available. The few anions which can parate directly (Cl, Br, I) behave in a similar way.

The following table shows that the values found by Le Blanc or normal solutions at 20°) for the polarisation of kathodes which values express intensities of fixation, agree well with ıe values of p given in *Table XV.*

TABLE XVII.

	p	k
$\longrightarrow Zn/ZnSO_4$ =	+0·521	+0·515
$Cd/CdSO_4$ =	+0·158	+0·160
$Cu/CuSO_4$ =	−0·582	−0·560
$Ag/AgNO_3$ =	−1·024	−1·055

f Le Blanc's theory is correct, the E.M.F. of the correspond-ing Daniell cells must be obtained by subtracting the two values of k.

TABLE XVIII.

Daniell element.	π calculated.	π found.
$Zn/ZnSO_4/CuSO_4/Cu$	1·075	1·096 (Jahn)
$Zn/ZnSO_4/CdSO_4/Cd$	0·355	0·360 (Braun)
$Cu/CuN_2O_6/Ag_2N_2O_6/Ag_2$	0·495	0·436 (Jahn)
$Cd/CdSO/CuSO_4/Cu$	0·720	0·680 (Le Blanc)

This comparison of the values of π agrees with the conclusion drawn above; hence Nernst's theory of current-production is confirmed in this way also.

The following experiment depends on the different intensities of fixation of the kations potassium and hydrogen, and suitable for the illustration of these differences. The flas (fig. 41) is filled to the level m n with a dilute solutio

vailable for the potassium ions; and the hydrogen ions of he sulphuric acid, the intensity of fixation of which is small, separate in proportion to the number of zinc ions which go into solution. Under these conditions the zinc continues to dissolve, when the circuit is closed, although it is not in contact with the sulphuric acid.

The dissociation theory attributes an independent existence to the ions of the electrolyte in the electrolyte; hence, if secondary reactions are eliminated, the potential difference, π, which it is necessary to communicate to the (indifferent) electrodes for the decomposition of the electrolyte, must just exceed the algebraic sum of the intensities of fixation. Now the intensities of fixation are equal to the quantities $\mathfrak{p}_1$ and $\mathfrak{p}_2$, that is, they are equal to those differences of potential which the positive and negative constituents of the substance to be decomposed would occasion on the electrodes, at the temperature and under the conditions of concentration that obtain at the time, were those constituents to assume the ionic condition. When π reaches this value, which is called the decomposition-tension, the needle of the galvanometer is deflected permanently. The ions separate on the electrodes in quantities which are proportional to the quantity of current, i, passing through the cell; and if W is the total resistance of the circuit, then

$$i = \frac{\pi - (\mathfrak{p}_1 + \mathfrak{p}_2)}{W}.$$

Le Blanc arrived at these propositions from the results of his researches. Although the supposition that all ions of one ind have the same intensity of fixation may not be free om objections, nevertheless that theory has the advanta- r others that it is able to explain the processes of ysis and polarisation. The theory may be illu: rimentally by electrolysing a series of normal so

[redacted]

[redacted]

[redacted]

theory of Le Blanc, especially when it is considered that temperature-coefficients have been overlooked in calculating the numbers in column 5.

With regard to the salts of those metals whose kations are un-ionised with greater difficulty than the ions of hydrogen, it is to be remarked that the electrolysis of dilute solutions of these electrolytes takes place with differences of potential smaller than the theoretical decomposition-tensions of the salts. In such cases it is not the metals, but hydrogen ions of water, that are set free at the kathode. Nevertheless, if the electrodes are sufficiently small, the current is of high intensity, and the tension is equal to the decomposition-tension, the metals separate from the dilute solution; for, under these circumstances, there is soon a deficiency of hydrogen ions in the neighbourhood of the kathode. It is even possible to bring about the separation of the metals of the alkaline earths from aqueous solutions of chlorides of these metals by the employment of currents of great intensity.

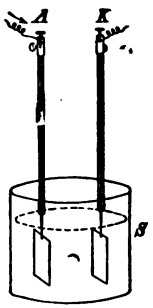


Fig. 42.

From what has been said it is evident that the kations will separate, at the kathode, from a mixture of electrolytes with a common anion in the inverse order of their intensities of fixation, when the tension at the electrodes of the electrolytic cell is gradually increased. This statement may be [illegible] by the following experiment. A solution containing [illegible]s copper sulphate, 110 grams ferrous sulphate, and [illegible]ulphuric acid, in 1000 grams water, is placed in [illegible] *S* (fig. 42); the platinum electrodes *A* and *K* [illegible]ms.) are immersed in this liquid at a dista[illegible] apart, and these electrodes are connected [illegible] battery of four accumulators, while a resist[illegible]

accumulators is passed through a resistance
and then through the cell, that part of the
which is immersed in the liquid is soon
a dull grey spot, about 3 to 4 centims.

broad, appears opposite the anode; and if this spot is gently pressed with an agate pencil, it assumes a metallic lustre, and shows a white spot of zinc, in the centre, about 1 centim. broad, surrounded by a yellow ring of brass. Scarcely anything but zinc has separated exactly opposite the anode, because the current is stronger in the immediate neighbourhood of this position, and the small quantities of copper were already deposited. But the farther any particular part of the basin is from the anode the less is the tension, the greater is the number of copper ions still in solution, and the greater is the quantity of copper deposited thereon. Thus it comes about that the exterior ring of metal remains copper-red during the brief duration of the experiment, whereas the inner ring consists of copper and zinc which form brass when pressed together.

The knowledge that the metals can be precipitated electrolytically one after another from a mixture of salts of heavy metals has met with important applications. Metallurgical chemists now employ electrolytic methods for the quantitative estimation of metals.* The electrolytic separation of metals has become still more important in the refining of copper, and the direct extraction of copper from its ores, for that is the only method which makes it possible to obtain this metal in sufficient quantities and purity for electrotechnical purposes. The refining of the crude copper obtained by metallurgical processes is conducted in baths of copper phate which are kept acid by sulphuric acid. Plates are le by melting the crude copper, which may contain as as 40 per cent. of impurities, and these plates serve odes; the kathodes are formed of thin sheets of

details see A. Classen's *Quantitative chemische Analys se* [Berlin, T. Springer, 1892].

[redacted]

the liquid surrounding the anode in the baths, in accordance with the equation

$$2FeSO_4 + SO_4 = Fe_2(SO_4)_3.$$

Höpfner employs a mixture of common salt and copper chloride solution for lixiviating the ores. Cuprous chloride is obtained in accordance with the equation

$$CuCl_2 + CuS = 2CuCl + S,$$

and this cuprous chloride remains in solution in the presence of the common salt. Copper chloride is re-formed in the neighbourhood of the anode, thus

$$2CuCl + Cl_2 = 2CuCl_2.$$

Höpfner's process has this great advantage that, because of the monovalency of copper in cuprous chloride, the quantity of metal precipitated in the baths is twice as great as that which is obtained by the same current in the process of Siemens. (*See* the experiments on Faraday's Law in *Chapter II., Part I.*)

CHAPTER VII.

IRREVERSIBLE CELLS.

WHEN zinc is placed in an acid, along with an electrode which dissolves very slightly or is altogether indifferent, and the circuit is closed, the greater solution-pressure of the zinc forces the hydrogen ions to discharge themselves at the indifferent electrode. The electricity is therefore led off from the electrode in question through the connecting wire. The current obtained from this cell is strongest immediately the cell is closed; but it soon decreases because of polarisation. For, on the one hand, the number of hydrogen ions of the electrolyte diminishes and the number of zinc ions increases; on the other hand, the internal resistance of the cell becomes greater, because the little bubbles of hydrogen adhere to the electrode which leads away the current; and, in the third place, an attraction comes into play between the adhering hydrogen and the anion of the electrolyte, whereby an electromotive force is produced which acts against the current.

The apparatus represented in figure 44 serves for the more detailed examination of these occurrences. A cylindrical roll of pure zinc, Z, to which the rod of zinc A is screwed on, is placed at the bottom of the vessel G (6 × 18 centims.) C is a plate of copper, pierced with holes like a sieve, and bent so as to be concave on the lower surface. The little rod

of copper s_1, s_2, s_3, and s_4 are riveted to the under surface, nd the copper rod K to the upper surface, of the copper late. The vessel G is filled with dilute sulphuric acid 1 : 15), and is then firmly closed by the cork P, through which ass the rods A and K, and also the exit-tube for gas R. When A and K are connected by a wire which is also in onnection with a moderately sensitive galvanometer, the eviation of the needle shows that K is the positive pole; nd, whereas the liquid between Z and C remains clear, the quid above C is turbid ecause of the little bub- es of hydrogen which se only from C. The adual falling off of the rrent is shown by the ow return of the needle wards the zero point, d also by the fact that e quantity of gas coming ough R, and collected a graduated cylinder, creases in each period five minutes.

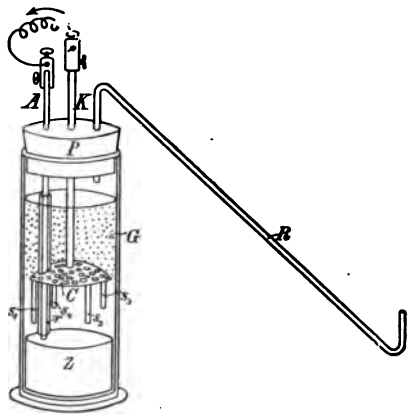


Fig. 44.

The internal resistance of the cell can be increased or inished considerably by raising or depressing the electrode contact with A being prevented by the glass tube r ough which A passes; and in accordance with this change internal resistance, the deviations of the needle, and the umes of gas which come off (5 to 15 c.c. in each five utes), vary also. One is able in this way to demonstrate dependence of the current strength on the resistar defined by Ohm's law, and also, although only appr ely, the validity of Faraday's law within a source

current. Finally, if the rod K is pressed downwards until the little rods s_1, s_2, s_3, and s_4 touch the zinc cylinder, the quantity of hydrogen reaches its maximum, and, because of the short-circuiting, the needle returns to the zero point. This phase of the experiment also illustrates the behaviour of pure and impure zinc towards acids, which has to be taken into account in the technical use of galvanic elements; for it shows that zinc, which when pure is insoluble (except at the moment of immersion) in dilute sulphuric acid at the ordinary temperature, must dissolve continuously in that acid when it comes into contact with, or is mixed with, traces of another metal.

When moderate currents are taken from cells the composition of which follows the type of the Daniell cell

$$Zn/ZnSO_4/CuSO_4/Cu,$$

no other changes occur except that the concentrations of the electrolytes vary somewhat by reason of the ionisation of the zinc and the un-ionisation of the copper ions. Cells of such a kind are unpolarisable, and their E.M.F. is *constant*. Moreover, the Daniell cells are *reversible*, inasmuch as if a current equal to the primary current is sent in the opposite direction into such cells, no other action except the re-establishment of the original concentration is effected. On the other hand, cells constructed like that described above, $Zn/H_2SO_4/Cu$, behave very differently. In these cells not only the electrolyte, but also the electrode which conducts away the current, is sensibly affected, in consequence of the solution of the zinc and the disengagement of hydrogen. These cells are *inconstant and irreversible*. The original state of affairs is not restored by passing a current in the opposite direction into one of these cells. The E.M.F. of the cell can no longer be ascertained by employing the equations of Nernst. Nevertheless, the

eral principles of the pressure-theory can be applied to lain the production of the galvanic current from these cells. he inconstant cells may be made constant by preventing separation of hydrogen at the electrode which conducts y the current. This is accomplished by oxidising the rogen to water, after it has given up its positive charge he kathode, by such oxidising agents as chromic acid,

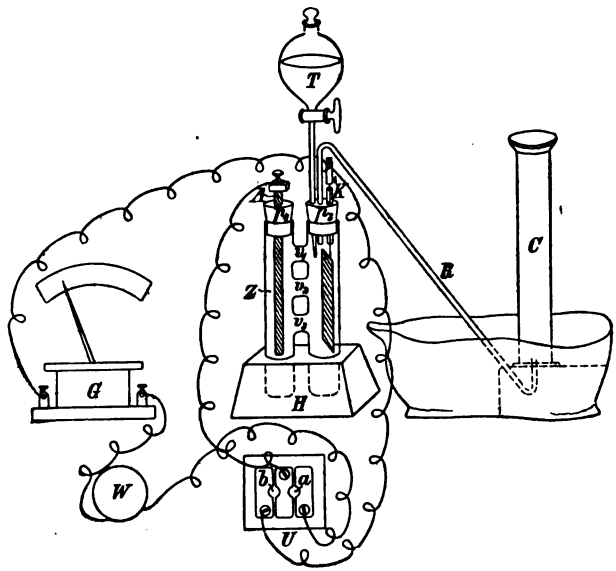


Fig. 45.

ic acid, peroxides, etc. *Not only is the polarisation overe by such secondary reactions, but the E.M.F. of these cells considerably increased.* For the greater part of the mical energy that is set free in the oxidation-process hanged into electrical energy, and the effect is the greater more energetic is the oxidation.

hese phenomena may be demonstrated in detail by the erimental arrangement represented in figure 45. The cell

Z is fastened into the wooden block H; the two limbs of the cell (2 centims. diameter) communicate by the cross-pieces v_1, v_2, and v_3. One of the limbs is closed by the cork p_1 through which passes the rod A, made of pure amalgamated zinc. The cork of the other limb, p_2, carries the platinum electrode K, the stoppered funnel T, and the tube for leading off gas R. The cell is completely filled with dilute sulphuric acid (1 : 8) by the funnel T, the narrow cylinder C is filled with water and placed over the end of the tube R, and the conducting wires are then arranged in the manner shown in the figure. Under certain circumstances it is necessary to connect a resistance coil, W, of about 500 ohms, with the galvanometer G. The galvanometer can be thrown into, or out of, the circuit by placing the key of the commutator U in a or in b. If the key is put into a, the needle shows a deviation of about seven degrees, but it soon returns some way towards zero. Small bubbles of hydrogen appear on K. If the key is now put into b, and the resistances of the galvanometer and the resistance-coil are thereby cut out, so much gas is given off that about fifteen bubbles rise per minute in C. After a few minutes the galvanometer is thrown into the circuit; the needle now moves through about five degrees only, because of polarisation. About 15 c.c. of a concentrated aqueous solution of chromium trioxide (1 : 1) are now allowed to flow from the point of the funnel T; this solution spreads through both limbs of the cell, and the evolution of hydrogen at once ceases, because the hydrogen is oxidised with formation of water and chromium oxide, as shown by the equation

$$2CrO_3 + 3H_2SO_4 + 3H_2 = Cr_2(SO_4)_3 + 6H_2O.$$

At the same time the needle very soon shows a deviation

about twelve degrees; and the same deviation is shown
r short-circuiting for an hour and a half. After the cell
been short-circuited for a couple of hours, the needle
s back to the tenth mark on the scale, because of the
dual using up of the oxidiser, and considerable quantities
chromium sulphate are now present in the electrolyte,
ich has become brownish black, and from which chromium
lroxide can be precipitated by adding ammonia.

Nitric acid behaves similarly to chromic acid; the nitric
l is reduced to the less oxidised compounds of nitrogen,
l when its concentration has become very small, and the
nent begins to be polarised, it is reduced finally to
nonium nitrate.

nasmuch as both these oxidisers are used as depolarisers
Bunsen cells, the experiment which has been described
uited for making clear the mode of action of these cells,
. the processes which occur in them.

The extent to which nitric acid and sulphuric acid mixed
h chromium trioxide are able to oxidise nascent hydrogen
be demonstrated more clearly by subjecting these acids
electrolysis in a U-tube (*see* fig. 12, p. 27). While the
sence of oxygen can be demonstrated in the limb
taining the anode, the kathode remains perfectly free
n gas, and occurrence of the changes which have been
icated can be detected in the acids that surround the
hode.

The apparatus represented in figure 46 is arranged so that
eral oxidising agents may be brought into the electrolyte
after the other, for the purpose of bringing about
olarisation at the kathode. The vessel *G* is fixed in
ring of a stand; the lower end of this vessel is closed
the cork *P* through which passes the conducting wi
of the horizontally placed copper disc *C*, which is

[redacted]

(3) A dilute solution of gold chloride placed on the platinum plate by means of a pipette; the gold is precipitated, after a few moments, as a lustrous deposit on the platinum plate.

(4) Crystals of mercuric chloride, silver nitrate, and potassium permanganate; these crystals are fastened by sealing wax on to glass rods, and are pressed on to the platinum disc for a moment only.

It is well known that solid oxidising agents, in the form peroxides of manganese and lead, act as depolarisers in clanché cells, and in accumulators.

In the Leclanché cell

$$Zn/NH_4Cl/\underbrace{MnO_2\ (carbon)}$$

c is the dissolving electrode; and a concentrated solution salammoniac is the electrolyte. The zinc dissolves in salammoniac solution, with evolution of hydrogen, bably in accordance with the equation

$$Zn + 2NH_4Cl = ZnCl_2.2NH_3 + H_2.$$

his process may be demonstrated by adding a little er to a mixture of ammonium chloride and zinc dust, g with a small quantity of iron powder, in a gas- ution flask, and collecting over water the gas which es off in considerable quantity at the ordinary tempera-

In the Leclanché cell the hydrogen is oxidised by manganese peroxide in the carbon cylinder;

$$H_2 + 2MnO_2 = H_2O + Mn_2O_3.$$

order to recognise the depolarising effect of manganese cide by an experiment specially arranged for tha ose, a piece of platinum foil, *A* (fig. 47), and a prism

be which just causes evolution of bubbles of hydrogen that is, which polarises the kathode. In order to test the capabilities of rods of carbon and manganese peroxide containing different quantities of the peroxide, a water-voltameter (of the U-form devised by Hofmann), with two platinum electrodes, a galvanometer, and an adjustable resistance, were included in the circuit of the apparatus represented in figure 47. By means of the galvanometer and the resistance, it was possible to maintain the current at a constant intensity for a long time. *Table XX.* gives a synopsis of the results of the measurements, and makes the way of working of a Leclanché element intelligible.

The numbers in columns 2, 5, 8, and 11 show that the depolarising effect of a kathode of carbon and manganese peroxide increases with increase of the quantity of peroxide, although the one increase is not directly proportional to the other, and that this effect gradually diminishes after the cell has been in use for a long time. The fact is also demonstrated that the Leclanché element gives a constant current only for a short time, but that after a longer time

TABLE XX.

6	7	8	9	10	11
With the same current of 0·072 ampères there were evolved in the following 25 minutes			In the next 75 minutes, until polarisation began, there were evolved		
in the voltameter	in the experimental apparatus	hence the MnO_2 fixed	in the voltameter	in the experimental apparatus	by a current of
·· H . O	4·60 c.c. H 6·19 c.c. O	61·06 per cent. H	9·40 c.c. H 4·70 c.c. O	0·50 c.c. H 4·30 c.c. O	·018 amp.
:· H c. O	4·47 c.c. H 6·35 c.c. O	68·03 per cent. H	12·86 c.c. H 6·43 c.c. O	0·69 c.c. H 5·52 c.c. O	·02
·. H . O	0 c.c. H 6·36 c.c. O	100·00 per cent. H	18·38 c.c. H 9·19 c.c. O	0·92 c.c. H 8·96 c.c. O	·0

of use it is polarised the more easily the less the quantity of manganese peroxide it contains. As the cylinders of carbon and peroxide in the elements that are used in the [German] Imperial telegraphic service contain, on the average, only 1·5 per cent. MnO_2, the current that is taken from such a cell should not exceed 0·07 ampères. If a stronger current is required, several cells must be arranged parallel to one another. The opinion which is sometimes expressed that the manganese peroxide of the carbon kathode is essentially superfluous is, therefore, erroneous, inasmuch as experiment shows that pure carbon has no depolarising effect.

Columns 4, 7, and 10 of *Table XX.* show that the volume of oxygen in the experimental apparatus continues to be somewhat less than that in the voltameter. This is explained by supposing that the manganese sulphate which is produced at the kathode diffuses into the anode-limb, and is there oxidised to $Mn_2(SO_4)_3$ or to some higher oxidised compound; for, as a matter of fact, the electrolyte near the anode soon assumes a rose-red coloration.

CHAPTER VIII.

ACCUMULATORS.

THE depolarising action of lead peroxide is much more effective than that of carbon-manganese peroxide; a mass of the former compound conducts the current metallically. Let a Hofmann's apparatus for the decomposition of water, and two apparatuses constructed in the manner shown in figure 47, be included in the circuit of a battery of twenty accumulators. The kathode of one of the two apparatuses is a prism of carbon-manganese peroxide containing 35·7 per cent. MnO_2, which is equivalent to 6·6 per cent. available oxygen; the kathode of the other apparatus is a prism cut from the lead peroxide plate of a Böse accumulator containing 51·8 per cent. PbO_2, which is equivalent to 3·3 per cent. available oxygen. After twelve minutes 62 c.c. hydrogen have come off from the platinum kathode of the apparatus for decomposing water, and 41 c.c. hydrogen from the carbon-manganese peroxide kathode. But the limb that contains the kathode of lead peroxide remains quite free from gas. The reason of this behaviour is found, partly in the structures of the two oxidising agents, for the mass of lead peroxide is much less dense than that of the carbon-manganese peroxide, and there are, therefore, many more points where the hydrogen ions are attacked by the oxidiser, and partly in the different rates of reaction,

for lead peroxide gives off oxygen more easily than manganese peroxide, as may be seen by heating the two substances in test-tubes. Whereas such a prism of carbon in manganese peroxide is polarised by a current of 0·05 ampères, the lead peroxide is able to sustain a current of four ampères without hydrogen being set free, that is without the E.M.F. of the accumulator being weakened by polarisation. This is, generally, the maximum quantity of current which can be taken from an accumulator that contains a single peroxide plate, and if greater quantities of current are required, several cells must be arranged in parallel to one another. The extraordinarily great depolarising action of lead peroxide explains why accumulators are so superior in steadiness even to Bunsen cells.

The foregoing experiment elucidates the processes which take place at the peroxide plate during the discharge of an accumulator, for the hydrogen is carried to that plate in the ionic state. The changes may be represented briefly by the equation

$$PbO_2 + H_2 = PbO + H_2O,$$

and the sulphuric acid then reacts on the lead oxide in accordance with the equation

$$PbO + H_2SO_4 = PbSO_4 + H_2O.$$

The processes that take place at the peroxide plate may be demonstrated by the use of a Hofmann's U-tube. In figure 48, *A* represents a prism cut from the lead plate of Böse accumulator,* and *K* is a platinum electrode. Dilu

* If such a lead prism (which is certainly very brittle) is not to be h a cylindrical rod of lead may be cast, and the surface increased cutting longitudinal channels. Before the experiment, the outer l must be changed to a spongy mass of lead by repeated oxid

sulphuric acid (1 : 5) is used as the electrolyte. The lead prism is reduced, in an appropriate way, before the experiment, by leading the current from two accumulators into the apparatus for about an hour, while the stopcocks remain open (the negative pole is to be connected with *A*). If the accumulators are then removed, the stopcocks closed, and *A* and *K* connected with a galvanometer, a current passes from *K* through the connecting wire to *A*. Hydrogen is produced in the reaction indicated by the equation

$$Pb + H_2SO_4 = PbSO_4 + H_2;$$

the hydrogen rises from the platinum kathode, and may be recognised by the turbidity it produces in the liquid. When the galvanometer is removed, about 20 c.c. of hydrogen collect in the kathode limb after sixty minutes. If the cell is left open for some time before it is short-circuited, little bubbles of hydrogen rise slowly from *A*; this indicates that the porous, spongy lead is able to occlude hydrogen, and to this circumstance may be ascribed the fact that the E.M.F. of an accumulator amounts to 2·4 volts shortly after the charging, while soon afterwards it sinks to somewhat less than two volts.

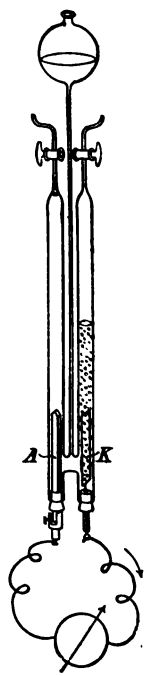


Fig. 48.

Accumulators are not only constant cells, they are also reversible cells, for they are constructed in such a way that it is possible to reverse the processes at both electrodes by leading currents into them in the reverse direction. The

and reduction, in a Hofmann's U-tube by Planté's method. The result is still better if, before this treatment, the channels are filled with a thic' pulp made by mixing red lead with sulphuric acid.

m-clock in action; it even suffices to decompose dilute phuric acid. If at least three cells, such as that shown figure 49, are prepared, and if they are charged and dis-arged several times, it can be shown that the quantity current obtained from them gradually increases. The lumes of gas, for instance, which are produced by dis-arging the cells through a water-voltameter, or the number minutes which the current is able to keep alight an candescent lamp (of about five volts), increase the more ie more often the charging and discharging of the cells performed.

If it is desired to charge a few ccumulators obtained from the nanufacturer for experimental use, or for some special practical pur-pose, and if neither the current from a dynamo nor a Gülcher's thermo-pile is at hand, the copper elements used in the [German] Imperial telegraphic service may be employed. These are constructed on the prin-ciple of the Meidinger cell, in the manner shown in figure 50. The vessel *g*, of one litre capacity, contains a thick-walled ring of zinc, *Zn*, which acts as the anode, and which is suspended from the rim of the vessel by three strips of zinc. The leaden plate *P*, into which is cast the rod of lead *s*, acts as the k- lc. The vessel is filled with water, in which about 20 zinc sulphate are dissolved, and about 100 grams of copper sulphate are placed on the bottom of the number of such cells is arranged in a proper way attery, which is fixed in a frame and kept at re mixing of the salt solutions may be avoided as

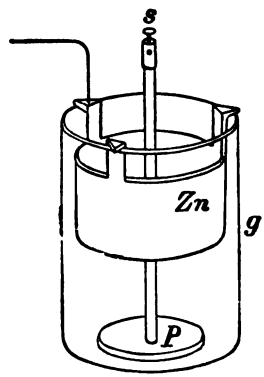


Fig. 50.

[illegible] are connected in the

[illegible] element is 1 volt, and its

nal resistance is 5 ohms, and if the opposing E.M.F. of ccumulator is 2·2 volts, then, neglecting the small internal stance of the accumulator, the intensity of the current from charging battery is

$$i=\frac{(12-[2\cdot2\times4])\,36}{5\times12^2}=\cdot16 \text{ ampère.}$$

w if the capacity of an accumulator amounts to 40 ampère-urs, then 80 ampère-hours must be obtained from the arging battery, because of the parallel combination of the o rows of accumulators. Hence the battery of accumu-ors will be charged in 80/0·16=500 hours. This example ows that the accumulators are storage-machines in the true nse of the word; for the electrical energy which gradually llects in them can be drawn off when required, either in mall quantities or in large quantities, which may amount to 2 volt-ampères in the foregoing case, at least for a short ime. Moreover, as 1 ampère separates 1·181 grams copper n one hour, and hence consumes 4·651 grams crystallised copper sulphate, and 1·213 grams zinc, the charging battery uses $3\times80/3\times12\times\cdot004651=4\cdot5$ kilos. copper sulphate, and 1·2 kilos. zinc, during the process of charging, in the example given.

Let m=the number of copper elements;
e=the E.M.F. of one of these elements;
w=the internal resistance of one of the copper elements;
p=the number of copper elements combined in series (in one of the rows);
n=the number of accumulator cells;
:the opposing E.M.F. of one of these accumulators;
=the number of accumulator cells combined series (in one of the rows);

then, neglecting the internal resistance of the accumulator cells, the battery of accumulators will be charged by a current of the intensity

$$i = \frac{(e\,p - \pi\,q)\,m}{w\,p^2} \text{ ampères.}$$

Now let an accumulator cell have the capacity of C ampère-hours; the charging current must supply $C \cdot n/q$ ampère-hours. Putting t as the number of hours required for charging, then—

$$i\,t = C.\frac{n}{q};$$

hence—

$$t = C \cdot \frac{n\,w}{m} \cdot \frac{p^2}{q(e\,p - \pi\,q)} \text{ hours.}$$

From this it follows that, when C, n, w, m, e, and π remain constant, t has a minimum value when

$$p = \frac{2\,\pi}{e} \cdot q,$$

and, in this case,

$$t = C.\frac{n\,w}{m} \cdot \frac{4\,\pi}{e^2}.$$

Hence, in order to charge as quickly as possible, the number of charging elements arranged in series ought to be about four and a half times the number of accumulator cells arranged in series in one of the rows.

It should be remarked, in regard to the zero effect of accumulators, that a distinction must be made between the quantity of current to be obtained from the accumulator, [illegible]pressed in ampère-hours, and is dependent on [illegible]f the active substance—the "active mass"— [illegible]l the peroxide, and the available energy of

rrent to be calculated in watt-hours.* In the best of accumulator the former amounts to 90 to 96 per and the latter only to 76 to 86 per cent. A small of the loss of energy, amounting to from 14 to 24 per is due to the transformation of a certain quantity of energy of the current into heat during the process of ging, but the greater part of the loss is dependent on fact that the opposing E.M.F., which has to be over- e by the charging current, amounts, on the average, 2·2 volts, whereas the mean E.M.F. of the charged ac- ulator is only 1·95 volts. The following example will ke the meaning of these two quantities clearer. An umulator is charged in eighteen hours with a current average intensity of which is two ampères, and the erage E.M.F. is 2·2 volts, and the accumulator is dis- arged in eight hours with a current of 4·25 ampères ean intensity and 1·97 volts average E.M.F. The quantity current obtained, expressed in ampère-hours, is

$$\frac{4{\cdot}25 \times 8}{2 \times 18} \times 100 = 94{\cdot}4 \text{ per cent.}$$

And the energy of the current, expressed in watt-hours, is

$$\frac{1{\cdot}97 \times 4{\cdot}25 \times 8}{2{\cdot}2 \times 2 \times 18} \times 100 = 84{\cdot}5 \text{ per cent.}$$

Although accumulators are much more constant, and of greater availability, than Bunsen cells, nevertheless their efficiency falls off when they are not used for several months. The lead slowly changes to lead sulphate, with evolution of hydrogen. This self-discharge goes on more

*If the comparison of the current with the conduction of water is adhered to, the ampère-hours will correspond to the quantity of water that flows away, and the watt-hours to the product of this quantity of water into the height of the fall [*compare* pp. 143, 144].

[illegible]

[illegible] three hours.*

[illegible] acquainted with the essential [illegible] the pamphlet by Dr. Karl Ebbs, [illegible].

CHAPTER IX.

THE ENERGETICS OF GALVANIC ELEMENTS.

ELECTRICAL energy possesses the great advantage that it can be stored easily, and can be changed into other forms of energy with but small loss.

Just as the mechanical work which a body falling freely is able to perform is measured by the product of the impelling force, which is conditioned by the height of the fall, into the mass of the body, so electrical energy is measured by the product of the difference of potential, π, into the quantity of current, i; that is to say, electrical energy is measured in volt-coulombs. And

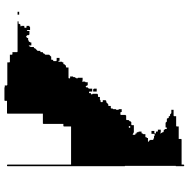
1 volt × 1 coulomb = 10^7 ergs = 0·2392 calories = 10,314 gram-centims.

When a galvanic element with the E.M.F. π, and the internal resistance w_1, is closed by a conducting wire the resistance of which is w_2, the whole of the electrical energy, $\pi \times i$, is changed into heat; and if the current circulates for t seconds with a constant E.M.F., this heat is expressed by the statement

$$C = 0{\cdot}2392\, \pi . i . t = 0{\cdot}2392\, i^2 (w_1 + w_2)\, t \text{ cals.}$$

The quantity of heat

$$c_1 = 0{\cdot}2392\, i^2 . w_1 . t \text{ cals.}$$



[illegible] along with 95 c.c.

[illegible] for 45 marks.

lphuric acid (1 : 4). The receiver R_2 contained an equal iantity of sulphuric acid; and this receiver was closed by cork which carried two copper wires connected with a latinum wire, p, 25 centims. long and 0·1 mm. thick, and aving a resistance of 2·5 ohms. When charged, the accuulator showed an E.M.F. of 1·9 volts, and an internal

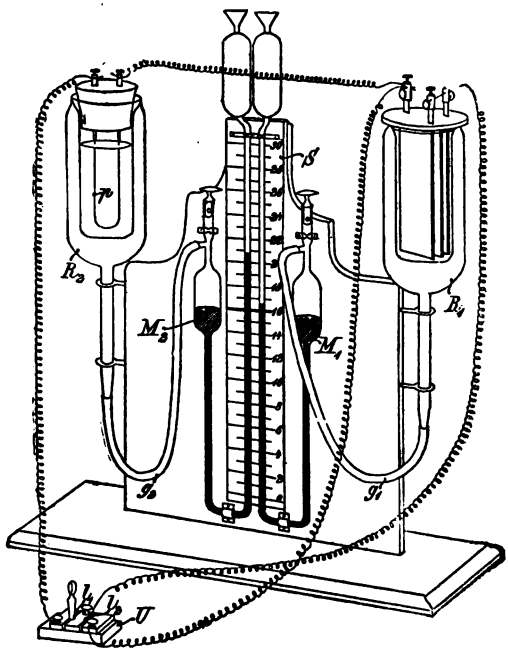


Fig. 53.

resistance of 0·15 ohm. When the liquids in the receivers had attained the temperature of the room, the wire for closing the circuit was adjusted in the way shown in figure 53 (the key of the switch U was placed in l_1). Under these conditions the quantity of current amounted to

$$i = \frac{1·9}{0·15 + 2·5} = 0·717 \text{ ampère.}$$

hemical energy of the element is changed into heat, for after hort-circuiting for one minute, the liquid in the manometer M_1 has risen through 20 mm.

Moreover, the galvanic current is capable of performing work of a specific kind in apparatuses included in the circuit: the work may be mechanical, such as driving an electromotor which raises a weight; or it may be chemical, such as electrolysing a conductor of the second class, and separating therefrom constituents which, taken together, possess a greater energy-content than the compound. *In such cases the total heat of the current must be smaller, by the energy-equivalent of such work.* This also may be illustrated by experiment. A cork is placed in the receiver R_2; this cork carries a manometer fitted with a three-way cock, and two wires attached to pieces of platinum foil 1 sq. centim. area, in the manner indicated in the cell Z in figure 40 (p. 175). If these electrodes are kept 1·5 centims. apart, the resistance of the cell is 2·5 ohms, and hence as great as that of the platinum wire p in figure 53. The E.M.F. of the accumulator suffices to decompose the sulphuric acid in the receiver R_2. After a minute, the liquid in the manometer of R_2 (the bore of the tube of which is 2 mm.) shows a difference of level of 30 centims. Putting the sum of the kathodic and anodic polarisation (*compare* p. 176) as 1·6 volts, the quantity of current which flows per second through the cross-section of the path of the current is

$$\frac{1{\cdot}9 - 1{\cdot}6}{0{\cdot}15 + 2{\cdot}5} = 0{\cdot}1132 \text{ coulomb};$$

and hence, if no chemical work is done in the receiver R_2, the total heat of the current, after twenty minutes, will be

$$C = 0{\cdot}2392 \times 0{\cdot}1132 \times 1{\cdot}9\,(0{\cdot}15 + 2{\cdot}5) \times 1200 = 61{\cdot}74 \text{ cals.}$$

...ELEMENT. ...

...ct of explosive ...
... for the ...
... in the ...
... with ...

... ...

... ... act free in the
... ... change is to ...
... ...

... ... connect the relation
... ... and the
... ... from which it ... makes its ...
... ... chemical energy ... more the longer it
... ... current, and the more lively are the
... ... cell, that is, the greater is the
... ... consumed in carrying on the process
... ... for a long time that, in accord-
... ... electrical energy which could
... ... to the loss of chemical
... ... chemical heat was equal
... ... the total circuit of the
... ... was not required to
... ... expresses the E.M.F.
... ... gram-atom of the
... ... is

... cals.

... of the chemical
... ...ion, then, accord-

the E.M.F. of a cell can be calculated directly from the
· of Q by the equation

$$\pi = \frac{Q}{n \times 23{,}090} \text{ volts.}$$

formula is found to be approximately accurate for the
$Zn/ZnSO_4/CuSO_4/Cu$. For in the process

$$Zn + CuSO_4 = ZnSO_4 + Cu$$

= 50,130 cals., because [Zn, O, SO_3Aq] = 106,090 cals., and
, O, SO_3Aq] = 55,960 cals. Hence it follows that

$$\pi = \frac{50{,}130}{2 \times 23{,}090} = 1{\cdot}09 \text{ volts,}$$

value agreeing with the mean value obtained by actual
asurements.

But considerable differences were discovered between the
emical heat and the current heat when other Daniell cells
re examined accurately, so that the rule of Thomson, that
, the assertion of the complete transformability of chemical
ergy into electrical energy, is found to have only an
proximate, and not a general, validity. More especially
is to be remarked that the E.M.F.s of the reversible cells
oved to be dependent on the temperature; they increase,
decrease, more or less with change of temperature. H. von
Helmholtz developed the following equation, on the basis of
the second law of thermodynamics, for the connection between
the absolute temperature T and the two quantities of energy,
the thermal energy and the energy of the current:—

$$n \times \pi \times 23{,}090 = Q \mp 23{,}090 \times n \times T \frac{d\pi}{dT}.$$

The expression $d\pi/dT$ here denotes the temperature-coefficient
of the cell, that is, the change of E.M.F. by a rise of 1°
of temperature. The product $23{,}090 \times n \times T \times d\pi/dT$ is

called the secondary heat, and it is equal to the difference between the current heat and the chemical heat. If $d\pi/dT$ is negative, that is, if the E.M.F. decreases with the temperature, then the electrical energy which is obtainable is less than the loss of chemical energy due to the chemical changes in the element. In this case the secondary heat is set free, besides the total heat Q, when a current is taken from the cell. On the other hand, if $d\pi/dT$ is positive, that is, if the E.M.F. increases with the temperature, the element gives a greater current energy than is equivalent to the consumption of chemical energy, and heat must be taken up from the surroundings, and converted into electrical energy, in order to keep the element at a constant temperature.

The accuracy of Helmholtz's equation has been completely verified by Jahn. A satisfactory agreement was found between the observed temperature-coefficients and those calculated from the values of π and Q which were determined by experiment.

A couple of examples will more fully elucidate Helmholtz's equation. In the cell

$$Pb/Pb(NO_3)_2/Ag_2(NO_3)_2/Ag_2$$

the following values were found for every 206·4 grams of lead dissolved at 0°:—

Current heat = 42,872 cals.
Chemical heat = 50,900 „

Hence the secondary heat is

$$23{,}090 \times 2 \times 273 \times d\pi/dT = -8028 \text{ cals.}$$

It follows that $d\pi/dT = -0{\cdot}000636$ volt; almost the same number was observed, namely $-0{\cdot}000632$ volt. Only 84 per cent. of the chemical energy was changed into electrical energy in this cell. The cell behaves like a steam-

ngine in which only a fraction of the heat set free by urning the coal is obtained as mechanical work.

The cell $Pb/Pb(C_2H_3O_2)_2/Cu(C_2H_3O_2)_2/Cu$ exemplifies the ase of a positive temperature-coefficient. In this cell Jahn ound

21,684 cals. for the current heat, and
17,533 „ for the chemical heat.

The value, calculated from the secondary heat, which is + 4151 cals., for $d\pi/dT$ is + 0·000329 volt, and the observed value was + 0·000385 volt. The fifth part of the energy of the current is derived from heat outside the cell. The cell transforms into electrical energy, not only the chemical energy of the processes that take place within it, but also a considerable quantity of heat from its surroundings, and in this respect it behaves like a volume of a gas which does work in expanding at the cost of the heat of its surroundings.

Galvanic elements for which the rule of Thomson holds good must have a very small temperature-coefficient, that is to say, their E.M.F. is only very slightly influenced by the temperature. This holds not only for the element $Zn/ZnSO_4/CuSO_4/Cu$, but also for the calomel element $Zn/ZnCl_2/Hg_2Cl_2/Hg$, which is a very suitable normal element* (E.M.F. is almost exactly one volt), the temperature-coefficients of which have been determined to be + 0·000034 and + 0·00007 volt respectively. The E.M.F. of a reversible cell can be calculated, by Helmholtz's equation, from the thermal value of the reaction which occurs, only when the temperature-coefficient is also known. It is especially interesting to carry out the calculation for accumulators, as Streintz has determined the temperature-coefficient of these

* The Clark element, which is most commonly employed as a normal element, $Zn/ZnSO_4/Hg_2SO_4/Hg$, has an E.M.F. at 15° of 1·4336 volts; ar its temperature-coefficient amounts to − 0·001 volt.

the two metals, and at that point only, and that this fference changes its sign according to the direction of :e current. This heating, or cooling, effect is called, from :e name of its discoverer, *Peltier's effect.* It is proportional) the first power of the intensity of the current, but it also epends, in a way not yet understood, on the substantive ature of the conductor. This effect is most clearly shown ;ith a rod made of antimony ınd bismuth, when the rod s sufficiently thick, and the :urrent is not too strong, so :hat the total heat, Q [as previously defined, p. 212], remains small. In figure 54 K is a globe of 4 centims. diameter; r is a tube, added to the globe, which is connected, by the caoutchouc tube s, with one of the manometers of the thermoscope represented in figure 53 (p. 209). The tubuluses t_1 and t_2 are closed by well-fitting corks, through which passes a rod, 8 mm. thick, made partly of antimony, *Sb*, and partly of bismuth, *Bi*, the two metals being melted together at l. The ends of the rod are connected with a battery of two accumulators, in the circuit of which a commutator is included, and also, if necessary, a resistance of 1 or 2 ohms. If the current passes from antimony to bismuth, the liquid in the manometer rises about 40 mm. in a few minutes, which signifies that the point of junction,

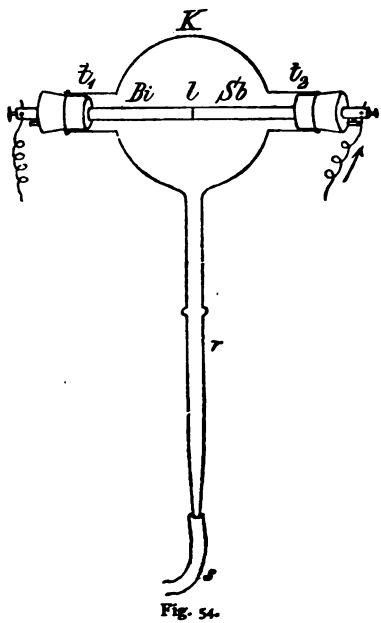


Fig. 54.

[redacted]

INDEX.

A.

Accumulators, 4 *note*, 197.
—— capacity of, 203.
—— charging with copper elements, 201.
—— chemical changes in, 198.
—— self-discharging, 205.
—— zero-effect of, 204.
Activity-coefficient, 69.
Alkali salts, electrolysis of, 17.
Aluminium-potassium chloride, 6.
Aluminium salts, electrolysis of, 7.
Amalgam-cells, 142.
Ammonia, electrolysis of, 24.
Ammonium chloride, electrolysis of, 24.
Ampère, definition of, 35 *note*.
Analysis by electrolysis, 183.
Aniline black, electrical preparation of, 31.
Anion, definition of, 3.
Anode, definition of, 3.
Avogadro's law applied to solutions, 116.

B.

ıg, electrical, 12.
›oints of electrolytes, 118.
Boiling point of a solution, 100.
—— —— molecular raising of, 104.
Brass, electrical formation of, 183.
Bunsen cells, 191.

C.

Calcium carbide, 8.
Calomel cell, 135.
Carborundum, 8.
Cells, amalgam, 142.
—— Bunsen, 191.
—— concentration, 128.
—— Daniell, 136, 141.
—— gas, 152.
—— inconstant, 188.
—— irreversible, 186.
—— Leclanché, 193.
—— liquid, 123.
—— reduction and oxidation, 146.
Chemical energy, change of, into electrical, 147, 151, 212.
—— —— in reduction- and oxidation-cells, 147.
—— —— relation of, to electrical energy, 211.
—— heat of galvanic elements, 215.
Chloride of nitrogen, preparation of, 24.

Dissociation theory of Arrhenius, 57, 60.
—— of water, 60.
Dropping electrode, 158.

E.

Electro-chemical equivalent, 35.
—— theory of von Helmholtz, 37.
Electrode, definition of, 3.
—— discharging, 129.
—— solution, 129.
Electrolysis, definition of, 3.
—— Grotthus's theory of, 66.
—— phenomena of, 4, 24.
Electrolyte, definition of, 3, 22.
Electrolytes, dissociation of aqueous solutions of, 117.
Electrolytic dissociation into ions, [illegible] 121.
—— solution of metals in mixtures 183.
—— solution - pressures of the metals 129, 157.
Electromotive force, 137. (See also *Potential-difference*.)
—— —— origin of, in a cell, 164.
—— —— dependence on temperature, 213.
—— series 165.
Electrometallurgy, 15, 26.
Energies of galvanic elements, [illegible]
—— of solutions, 89.
Energy, chemical, change of, into electrical energy, 147, 151, 212
—— of current, change of, into chemical energy, 211.
—— —— change of, into heat, 38, 211.
—— contents of ions, 65, 68.
Eosin, dissociation of, 61.

Etching, electrical, 15, 16.
Ethereal salts, saponification of, 69.

F.

Faraday's law, 32.
Fixation of ions, intensity of, 171, 176, 181.
Freezing points of electrolytes, 118.
—— —— of solutions, 107.
—— —— molecular lowering of, 109.

G.

Galvanic current, comparison of, with conduction of water, 143.
Gas-accumulators, 154.
Gas-cells, 152.
Gaseous equation, 84.
Gold, electrical extraction of, 26.

H.

Helmholtz's energy equation, 213.
Hittorf's transport-numbers, 41.
Hydrochloric acid, electrolysis of, 11.
Hydrogen ions, charges on, 39.
—— —— velocity of migration of, 56.
—— peroxide, electrical production of, 23.
—— position of, in electromotive series, 166.
Hydroxyl ions, velocity of migration of, 51.

I.

Inconstant cells, 188.
Inlaying metals, 16.
Intensity of current, measurement of, 35.
—— of fixation of ions, 171, 176, 181.
Iodoform, electrical preparation of, 30.
Ionisation, heat of, 63.
—— coefficient, 59 *note*, 69.
Ions, complex, 24, 62.
—— conception of, 3.
—— energy-contents of, 65, 68.
—— migration-velocities of, 51, 53.
—— proof of free, 71.
Iron, galvanised, 170.
—— tinned, 169.

K.

Kanarin, electrical preparation of, 30.
Kathode, definition of, 3.
Kation, definition of, 3.
Kohlrausch, law of, 45.

L.

Lead chloride, electrolysis of, 8.
—— solutions, electrolysis of, 25.
Leclanché cells, 193.
Liquid cells, 123.
Litre-atmosphere, definition of, 85.

M.

Magnesium, electrical preparation of, 4.
—— potassium chloride, preparation of, 4.
Mercurous chloride cell, 135.
Mercury unit, 46.

Metals, inlaying of, 16.
—— colouring of, 25.
—— electrolytic estimation of, in mixtures, 183.
Methylene blue, dissociation of, 62.
Migrations of ions, velocities of, 51, 53.
Molecular weights, determination of, by boiling-point method, 105.
—— —— —— by freezing-point method, 109.
—— —— —— by vapour-pressure method, 96.

N.

Neutralisation, heat of, 71.
Nitration, rate of, 50.
Nitric acid, electrolysis of, 191.
Normal element, 215.

O.

Occlusion by lead, 199.
—— by palladium, 151, 166.
Ohm, definition of, 35 *note*.
Organic compounds, electrical preparation of, 29.
Osmotic work of solutions, 90.
—— pressure, analogy between, and gaseous pressure, 89.
—— —— connection between, and vapour-pressure, 97.
—— —— definition of, 76.
—— —— demonstration of, experimentally, 77.
—— —— magnitude of, 77, 91.
—— —— measurements of, 78, 80.
—— —— Pfeffer's laws of, 84.
—— —— van't Hoff's law of, 85, 88.
Osmotic theory of the formation of the current, 122—218.
Oxidation- and reduction-cells, 146.
Oxygen, preparation of, by electrolysis, 16.
Ozone, formation of, by electrolysis, 23.

P.

Palladium, occlusion of hydrogen by, 151, 166.
Peltier's effect, 217.
Plasmolysis, 77.
Polarisable electrodes, 173.
Polarisation, 41, 191.
Poles, positive and negative, 18.
—— reagent for detecting, 19.
Positive and negative poles, 18.
—— current, direction of, 129.
Potassium chlorate, electrical preparation of, 13.
—— ferrocyanide, electrolysis of, 27.
—— hydroxide, electrolysis of, 8.
—— ions, velocity of migration of, 51.
—— sulphate, electrolysis of, 18.
—— sulphocyanide, electrolysis of, 29.
Potential-difference between a metal and an electrolyte, 130.
—— of concentration-cells, 128.
—— of Daniell cells, 136, 160, 164, 177.
—— of liquid cells, 123.
—— measurement of, by compensation method, 137.
—— —— by dropping electrode, 159.
Purification, electrical, of organic substances, 60.
—— —— of copper, 183.

R.

Reactivities of dissociated compounds, 69.
Reduction- and oxidation-cells, 146.
Resistance, measurement of, in electrolytes, 45.
Reversible cells, 188.

S.

Salt, Berzelius' definition of, 20.
—— Daniell's definition of, 21.
—— Hittorf's definition of, 22.
Salts, double, 70.
Secondary heat of galvanic elements, 214.
—— processes of electrolysis, 24.
Semipermeable membranes, 77.
Silver ions, velocity of migration of, 56.
Silvering, electrical, 15, 26.
Sodium acetate, electrolysis of, 28.
—— chloride, electrolysis of, 10, 12.
—— ions, velocity of migration of, 56.
Solution-pressures of metals, 129, 157.
Solutions, energetics of, 89.
—— of electrolytes, 117.
—— van't Hoff's theory of, 74.
Stannous chloride, electrolysis of, 148.
Sulphuric acid, electrolysis of, 17, 22.

T.

Temperature-coefficient of galvanic elements, 213.
Thermoneutrality, 70.
Tin on iron, 168.
—— tree, 10, 134.
Transport-numbers, 41.

U.

Units, electrical, 35 *note*, 46.
Unpolarisable electrodes, 172.

V.

Valency-charges of ions, 37.
Vapour-pressure, molecular depression of, 93.
Vapour-pressures of solutions, 92.
—— —— connection between, and osmotic pressure, 97.
—— —— laws of, 93.
—— —— —— deduction by van't Hoff's equation, 97.
—— —— proof of, 94.
Volt, definition of, 35 *note*.
Voltameter, 33.

W.

Water, electrolysis of, 22, 60.
—— molecular conductivity of, 60.
Watt, definition of, 35 *note*.

Z.

Zinc on iron, 170.
—— chloride, electrolysis of, 9.

Printed by Hazell, Watson, & Viney, Ld., London and Aylesbury.

H. GREVEL & CO.'S PUBLICATIONS.

THE CLASSICAL PICTURE GALLERY.

Reproductions of Classical Pictures from the Public and Private Galleries of Europe.

Published Monthly.

Containing Twelve Plates each. Each Part, 1*s*. 4to.

Annual Subscription, 15*s*. post free.

"The reproductions are marvellously cheap, and they certainly give a far better idea of the pictures represented than any publication we have seen. To those who have an interest in art, to whom pictures in foreign galleries are mere names, the work will be most valuable; nor will it meet a less cordial welcome from those who desire to recall what they have seen."—*Graphic.*

THE CLASSICAL SCULPTURE GALLERY.

Reproductions of Classical Sculptures from the Public and Private Collections of Europe.

Published in 12 *Monthly Parts, containing* 12 *Plates each.*
Each Part 1*s*. 4*to*.

Annual Subscription, 15*s*. post free.

"Messrs. H. Grevel & Co. have commenced the issue of a Classical Sculpture Gallery of reproductions by the autotype process. Sculpture lends itself particularly to this method of reproduction, and the work, to judge by the prints that have been forwarded, should have a high technical and educative value."—*Edinburgh Evening News.*

THE PRINT GALLERY.

Reproductions of the Masterpieces of Engraving from the end of the Fifteenth to the beginning of the Nineteenth Century.

With Biographical and Explanatory Notices.

Published in Monthly Parts, containing 8 *Plates each.*
Each Part, 1*s. Fol.*

Annual Subscription, 15*s.* post free.

"Some of the finest art in the world has been expressed in line work, and Messrs. Grevel & Company, London, have just commenced the monthly issue of a series of reproductions of those masterpieces. They will date from the end of the fifteenth to the beginning of the nineteenth century. The first number, which is at a popular price, promises well. The rendering of tone values is excellent.—*Edinburgh Evening News.*

"For artistes and art students we cannot conceive any more useful aid to study."—*Star.*

CORRESPONDENCE OF WAGNER AND LISZT.

Translated into English, and with a Preface by Dr. FRANCIS HUEFFER.

New Edition, Revised. With a full Index by W. ASHTON ELLIS.

Portrait. 2 Vols. Crown 8vo, cloth, gilt top. £1 1*s.*

"A new edition of Dr. Hueffer's excellent translation of the correspondence of Wagner and Liszt will be welcome, not only to musical enthusiasts, but also to every admirer of the fast-decaying art of letter-writing. For the letters, besides being of signal interest from a biographical standpoint, are equally valuable for their own qualities of lucidity, frankness, and charm. They form two most attractive volumes, and are published at a reasonable price in a decent and self-respecting *format.* The new edition has been supervised by Mr. Ashton Ellis, who has not found it necessary to add much to Dr. Hueffer's labour. The most important of Mr. Ellis's services, however, is the addition of an index—always a difficult thing to prepare, and particularly difficult in a case like the present, where subjects and allusions, rather than mere names, are the chief items to be tabulated. It was, indeed, Dr. Hueffer's expressed desire that the letters should eventually be indexed ; and in undertaking the task Mr. Ellis has set himself to complete the original scheme of the translation."—*St. James' Gazette.*

WAGNER'S LETTERS TO HIS DRESDEN FRIENDS

(Uhlig, Fischer, Heine, etc.).

Translated by J. S. SHEDLOCK.

With an Etching of WAGNER'S PORTRAIT by C. W. SHERBORN, and a COMPLETE INDEX.

Crown 8vo, cloth extra, gilt top. 10*s.* 6*d.*

"All who are interested in the personal character and career of Richard Wagner—such persons may hold diverse opinions as to his art—will welcome this book as a companion volume to the English version of the Correspondence between Wagner and Liszt."—*The Musical Times.*

"It is quite impossible within limited space to give a satisfactory description of the contents of this extremely interesting volume."—*Athenæum.*

"These letters are supremely interesting, for they show Wagner as he really was, no one-sided representation, but the whole man."—*Daily Telegraph.*

WAGNER AND HIS WORKS:

The Story of His Life, with Critical Comments.

By HENRY T. FINCK.

With Two Portraits. 2 Vols. Crown 8vo, cloth. £1 1*s.*

"Mr. Finck has undoubtedly enriched the literature of Music with a book of sterling worth."—*Morning Post.*

"Mr. Finck has an exhaustive acquaintance with all the works on the subject, he has Wagner's own works at his fingers' ends, and he has shown remarkable ability in digesting and summarising his plethora of material. More than that, his comments are expressed in a lively and entertaining style."—*Graphic.*

"Mr. Finck's work is perhaps the most exhaustive and appreciative account of the great composer that has appeared in the English language." —*Times.*

LETTERS OF FRANZ LISZT.

Edited and collected by LA MARA.
Translated by CONSTANCE BACHE.

Vol. I. Years of Travel as Virtuoso.
Vol. II. From Rome to the End. With a Frontispiece.

2 vols. With a Portrait. Crown 8vo, cloth, £1 1*s*.

"Between six and seven hundred letters, every one of which is worth reading, are reproduced in this collection, and are lavishly supplemented by Chronological and Explanatory Notes, which render the book extremely valuable to musicians and men of letters as a work of reference. Its technical production, moreover, is in every respect exemplary."—*Daily Telegraph.*

"Altogether the letters present a lifelike study of an original, amiable, and singularly interesting character, and they may be said to shed a new light upon the labours, struggles, and triumphs of one who was for many years the petted but never the spoiled darling of society, and who, both as maestro and virtuoso, had the gift beyond any man of his period of exciting the personal affection, as well as the enthusiastic admiration, of all with whom he came in contact."—*Birmingham Daily Post.*

CELEBRATED PIANISTS OF THE PAST AND PRESENT.

By A. EHRLICH.

A Collection of 116 Biographies and 114 Portraits.
8vo, cloth, 7*s*. 6*d*.

"A convenient record of important biographical details. Over one hundred masters and mistresses of the keyboard find places in these pages —the names ranging from John Sebastian Bach to Couperin and Rameau, down to the most famous among contemporary executants."—*Daily Telegraph.*

MANUAL OF MUSICAL HISTORY.

With 150 Illustrations of Portraits, Musical Instruments, Facsimiles of Rare and Curious Musical Works.

By JAMES E. MATTHEW.

Crown 8vo, cloth. 10*s*. 6*d*.

"This book is well written, interspersed now and again with an anecdote or amusing passage in the lives of the great composers."—*Morning Post.*

"The sketch of the later music in Germany, Italy, France, and England, brings the book up to date, and concludes a well-written, profusely illustrated, and admirably compiled volume."—*Musical News.*

"The plan of the book is admirably arranged and printed. The work can be well recommended to all who desire a musical history, giving full information in a concise and accessible form, and which is detailed without being diffuse."—*Musical Standard.*

VELASQUEZ AND HIS TIMES.

By CARL JUSTI, Professor at the University of Bonn.

Translated by Professor A. H. KEANE, and Revised by the Author.

With 52 magnificent Woodcuts, an Etching of Velasquez' Own Portrait by Forberg, and a Plan of the Old Palace at Madrid.

Royal 8vo, Roxburghe. £1 1*s.*

"No complete or adequate account of the life and works of Diego de Silva Velasquez has been written until the masterly Biography by Professor Carl Justi, which will long be looked upon as *the definitive biography* of the Great Master."—*Edinburgh Review.*

"No better example could be given of the growth of historical knowledge during the past thirty years than is to be found in Carl Justi's recent book on 'Velasquez,' well translated by Professor A. H. Keane. The amount of research and of real observation which his book shows is typical of the modern scholar."—*Times.*

MANUAL OF EGYPTIAN ARCHÆOLOGY: And Popular Guide to the Egyptian Antiquities for Students and Travellers.

By Professor G. MASPERO, D.C.L. Oxon.

English Edition, with Notes, by AMELIA B. EDWARDS, Ph.D., LL.D.

With 309 Illustrations.

New and Cheaper Edition, revised by the Author.

CONTENTS.—Chapter I. Civil and Military Architecture. Chapter II. Religious Architecture. Chapter III. Tombs. Chapter IV. Painting and Sculpture. Chapter V. The Industrial Arts.

Crown 8vo, cloth extra, gilt top, 6*s.*

"It is a marvel of erudition and condensation. It sums up the long results of thousands of years of Egyptian civilisation in language precise enough to make the work a handbook for the specialist, and popular enough to insure its becoming a guide to the antiquarian lore of the country for travellers in Egypt."—*Scotsman.*

"The Publishers have conferred a boon alike on tourists and students by their issue of a fourth and revised edition of Professor Maspero's 'Manual of Egyptian Archæology,' as translated by the late Miss Amelia B. Edwards. In its essential features, which could not indeed be easily improved, the work remains what it was when first presented to the English public some eight years ago, but the present edition has been carefully corrected, in view of the continued progress of Egyptological knowledge, by M. Maspero himself; additional matter has been inserted, and numerous fresh illustrations are given. It should also be mentioned that by the introduction of separate page-headings and other improvements the worth of the book for purposes of reference has been considerably enhanced."—*The Guardian.*

H. GREVEL & CO., 33, KING STREET, COVENT GARDEN, LONDON, W.C.

THE ANCIENT EGYPTIAN DOCTRINE OF THE IMMORTALITY OF THE SOUL.

By DR. A. WIEDEMANN,
Professor of Oriental Languages at the University of Bonn.
With 21 Illustrations.

Crown 8vo, cloth. 3*s.*

"Professor Wiedemann's treatise is quite a perfect thing of its kind. He treats his fascinating subject with marvellous clearness, and the reader follows his guidance through the mazes of the great system of immortality with breathless interest."—*Saturday Review.*

"Prof. Wiedemann's little book appeals not only to the Egyptologist, but also to the student of religion and history, as well as to that larger public which is interested in all that relates to the thoughts and beliefs of civilised men, when set forth in lucid language by a skilful and learned interpreter. Henceforward it will be impossible not to have a clear idea of what the old Egyptians meant when they spoke of *ka* the double, of *ba* the soul, of *ab* the heart, of *sâhu* the idealised body or human form, of *khaîb* the shadow, and of the 'Osiris' of the dead man himself."—*Academy.*

RELIGION OF THE ANCIENT EGYPTIANS.

With 73 Illustrations from the Monuments.

By ALFRED WIEDEMANN, Ph.D., Professor in the University of Bonn.

Author of "Aegyptische Geschichte," "Herodot's Zweites Buch," "Ancient Egyptian Doctrine of Immortality," etc.

Demy 8vo, Cloth extra. Price 12*s.* 6*d.*

This MANUAL OF EGYPTIAN MYTHOLOGY is based on the original texts, references to which are given in the footnotes. It is carefully illustrated; and a full index facilitates reference, especially in the case of deities that receive only isolated or incidental notice.

The work is also a description of Egyptian religious thought and belief prevailing in historic times.

The author is well known throughout Europe for his valuable writings on the history and mythology of Ancient Egypt, and for his exhaustive knowledge of the literature bearing upon his subject.

This work is the only Manual of Egyptian Mythology hitherto published in England.

EXCURSIONS IN GREECE TO RECENTLY EXPLORED SITES OF CLASSICAL INTEREST

(Mycenæ, Tiryns, Dodona, Delos, Athens, Olympia, Eleusis, Epidauros, Tanagra).

A Popular Account of the Results of Recent Excavations for Students and Travellers.

By CHARLES DIEHL, Professor at the University of Nancy.

Translated by EMMA R. PERKINS,

Illustrated. Crown 8vo, cloth. *7s. 6d.*

"It would be difficult to point to a single volume in English which takes so comprehensive a survey or deals with its materials in a manner at once so scientific and so popular as this work of M. Diehl."—*Times.*

"We are carried round Greece by a very entertaining and well-informed guide."—*Academy.*

"A book of considerable value to the English student of classical archæology."—*Saturday Review.*

"Of the volume in general we may say that it is of the very greatest value."—*Pall Mall Gazette.*

THE OLYMPIC GAMES.

B.C. 776—A.D. 1896.

Published with the sanction and under the patronage of the Central Committee in Athens.

By SP. P. LAMBROS and N. G. POLITES, Professors at the University of Athens.

Part I.—THE OLYMPIC GAMES IN ANCIENT TIMES, with 101 Illustrations;

Part II.—THE HISTORY OF THE REVIVAL OF THE GAMES. Participators, Competitors, Victors. Description of the Festival at Athens.

With English and German Text, in an elegant cover, 2 Parts. 4to, *10s.*

H. GREVEL & CO., 33, KING STREET, COVENT GARDEN LONDON, W.C

[illegible]

MANUAL OF ARCHÆOLOGY

[illegible]

[illegible]

[illegible]

Crown 8vo. cloth, 6s.

[illegible]

[illegible]

[illegible]

[illegible] STREET, COVENT GARDEN, LONDON, W.C.

THE EGYPTIAN STRUWWELPETER;

OR

The Struwwelpeter Papyrus.

With Full Text and 100 Original Vignettes.

From the Vienna Papyri.

Respectfully Dedicated to Children of All Ages.

4to boards. 3*s*. 6*d*.

"A delightful children's book, in which the various discoveries in Egyptian antiquity are most amusingly parodied in the well-known style of the original Struwwelpeter, for the benefit of the rising generation. Both the letterpress and the illustrations are wonderfully humorous, witty and diverting, and the skill with which the characteristics of Egyptian mythology are made to take their place in the divertissement of the whole is quite extraordinary. The book is altogether delightful, and is sure to approve itself to a discerning public."—*The Bookseller.*

THE BOOK:

Its Printers, Illustrators, and Binders, from Gutenberg to the Present Time.

By HENRI BOUCHOT, of the National Library, Paris.

With a Treatise on the Art of Collecting and Describing Early Printed Books, and a Latin-English and English-Latin Topographical Index of the Earliest Printing Presses.

Containing 172 Facsimiles of Early Typography, Book Illustrations, Printers' Marks, Bindings, numerous Borders, Initials, Head- and Tail-Pieces, and a Frontispiece.

Royal 8vo, vellum cloth. £1 1*s*.

"Beginning with the Block Books, which anticipated by a few decades the discovery of Printing, this work gives an account of the rise and progress of Printing, the dispersion over Europe of the German printers, the growth of Book Illustration, of the Binder's Art, and all similar matter down to the present day."—*Athenæum.*

H. GREVEL & CO., 33, KING STREET, COVENT GARDEN, LONDON, W.C.

MANUAL OF BIBLIOGRAPHY:

A Short Account of the Knowledge of the Book, Library Management, and the Art of Cataloguing.

With 57 Illustrations.

By [illegible] Inner Temple Library. New Edition, [illegible] crown 8vo, cloth. 5s.

[illegible] the bookbinder, the artist, the author, [illegible] will all turn with interest, and, we venture [illegible]. It describes 'The Invention and [illegible] of 'The Book,' 'The Ornamenta- [illegible] and the Catalogue,' and kindred topics. [illegible] a glossary, and an index are added. [illegible] the illustrations add to its beauty and

---

[illegible] BOOK-PLATES.

[illegible] Designs for Ex-Libris, Con- [illegible] the Little Masters of [illegible] by Joseph Sattler.

[illegible] in Portfolio. £2 2s. net.

[illegible] s interesting and so curious as the [illegible] were, quaint, picturesque, [illegible] he no limit to his inven- [illegible]

[illegible] our subject which has yet

[illegible] Year-Book.

[illegible] BOOK-PLATES

[illegible] containing 100 Plates [illegible] by Artists, chiefly H. S. Beham, [illegible] etc.

[illegible] net.

[illegible] specimens of the engraver's [illegible] an epitome [illegible] greater care is [illegible] several English [illegible] with anything [illegible] Plates by Mr. [illegible] other artists, have just [illegible] fairness, and common [illegible] effect."

[illegible] W.C.

OLD SWORD PLAY.

By Capt. ALFRED HUTTON.

Author of "The Swordsman," "Cold Steel," and "Fixed Bayonets," etc.

With 58 Illustrations after Alfieri, Angelo, Di Grassi, Liancourt, Marozzo, De la Touche, Weischner, and other celebrated Fencing Masters, containing a Series of Studies of the Swordsmanship of the 16th, 17th, and 18th Centuries, embracing the Two-hand Sword, Rapier, and Dagger, Broadsword and Buckler, "Case of Rapiers," Early Small Sword Play, etc.

Royal 8vo. Superfine Dutch paper. Vellum cloth, extra. (Limited to 300 copies.)

Buckram. £1 1*s.*

"Captain Hutton has compiled and arranged the lessons in his book so as to make the antique methods accessible to the student without the labour of searching through many ancient volumes."—*Graphic.*

"Captain Hutton's clear and concise treatment of this curious form of Sword Play, illustrated as it is by plates from Marozzo and Di Grassi, is extremely interesting. This latest contribution to the literature of fencing should not be neglected by any one interested in that fine art."—*Illustrated London News.*

THE SWORDSMAN:

A Manual of Fence for the Foil, Sabre, and Bayonet. With an Appendix consisting of a Code of Rules for Assaults, Competitions, etc.

By ALFRED HUTTON, late Capt. King's Dragoon Guards, Author of "Cold Steel," "Fixed Bayonets," etc.

With 42 Illustrations.

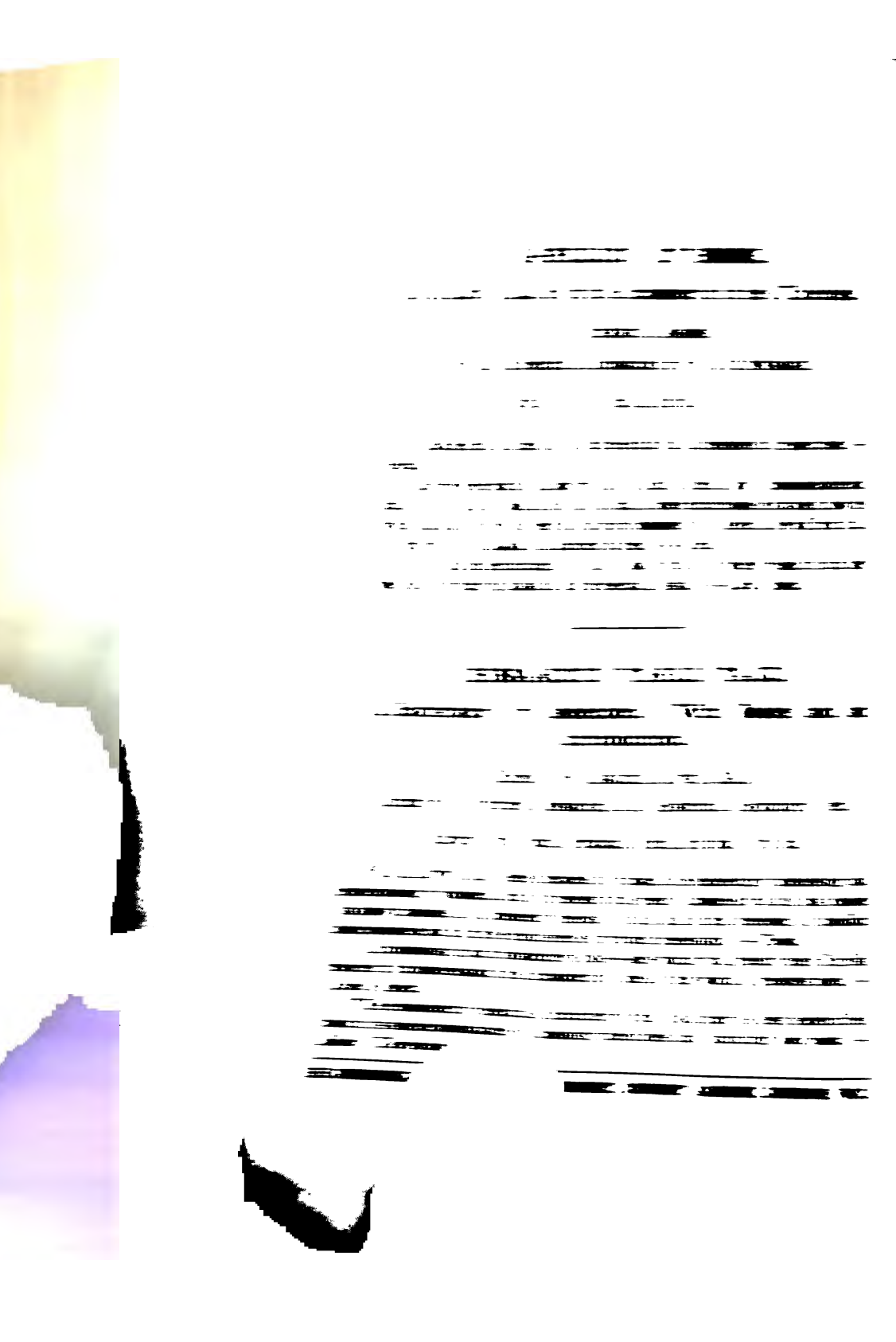
Crown 8vo, cloth. 3*s.* 6*d.*

50 copies printed on Whatman paper, bound in vellum at 10*s.* 6*d.*

"Captain Alfred Hutton, a well-known authority on the subject, has compiled a book, which should prove of much service to the beginner, and which also contains many useful hints to the more accomplished performer."—*Morning Post.*

"Books of the kind are rare in English, and as Captain Hutton is a skilled master, and his method carries authority, the book deserves a welcome from all who are interested in the maintenance of good swordsmanship."—*Scotsman.*

H. GREVEL & CO., 33, KING STREET, COVENT GARDEN, LONDON, W.C.



THE STUDENT'S ATLAS OF ARTISTIC ANATOMY,

For the Use of Sculptors, Painters, and Students.

With THIRTY-FOUR PLATES.

By CHARLES ROTH, Professor of Sculpture at the Munich Academy.
Edited by C. E. FITZGERALD, M.D.

Fol., in Portfolio. £1 5*s*.

"Professor Roth's well-known and highly valued plates of the human muscles and bones, with his nomenclature and descriptive notes, are worthily reproduced in this complete portfolio."—*Athenæum.*

"The plan of the Atlas, which has been considerably enlarged from its original form, is very simple and convenient. The two first plates represent the bony framework of the body, and the eight following ones the muscles in action. The figure plates are carefully drawn and admirably printed, and each is followed by an explanatory plate, in which the parts depicted are numerated, while notes are added directing attention to those points which are of especial interest to artists."—*Daily Graphic.*

"The plates are admirably executed, the engraving being smooth and even, and at the same time sufficiently vigorous in the contrast of light and shade. Dr. Fitzgerald's translation of Professor Roth's work is altogether a valuable aid to the study of artistic anatomy, and in itself a work of art."—*Lancet.*

MY WATER CURE.

Tested for more than 35 Years for the Cure of Diseases and the Preservation of Health.

By the Rev. SEBASTIAN KNEIPP,
Parish Priest of Wœrishoven, Bavaria.

With 100 Illustrations and a Portrait of the Author.

Complete Copyright Edition. Enlarged by 136 pages; translated from the last (the 36th) German Edition.

Entirely revised by the Author, with 50 additional Illustrations of Medicinal Plants.

8vo, cloth, 396 pp. 6*s*.

"All Germany bears witness to the worth of his regimen."—*The Guardian.*

"THUS SHALT THOU LIVE!"

Plain and concise advice for the Healthy and the Sick on a practical rational Mode of Living and a natural Method of Curing

By [illegible] Kneipp, Founder of Wörishofen (Bavaria).
Translated from the last German Edition.
By [illegible].

[illegible] on the Principles and Means of Preserving It.
[illegible] How to Live in Health after Kneipp's Method.
[illegible] Water in Disease.

"[illegible] contains an immense amount of good advice [illegible] Father Kneipp writes [illegible] hardening of [illegible] system generally."—*Echo.*

MY WILL. A LEGACY TO THE HEALTHY AND THE SICK.

By Father Kneipp.

Containing Father Kneipp's final directions for the application of his Water Cure at Home.

With 39 Photographs taken from life, and other Illustrations. 8vo, cloth. 6s.

"In 'My Will' are given full particulars of how to administer baths of [illegible] instructions as to bandages and compresses, a list of diseases [illegible] and finally, details as to the preparation of his herbal teas. [illegible] etc. There is a simplicity about this system which [illegible]."—*The Westminster Gazette.*

FATHER KNEIPP'S PLANT-ATLAS.

Describing, and Picturing True to Nature all Medicinal Plants mentioned in Father Kneipp's Books.

With [illegible] containing 69 specimens.

[illegible] with uncoloured Plates, 7s. 6d.

[illegible] the "Plant-Atlas," to find [illegible] to look for in woods or fields, [illegible] way, that "Family Medicine-[illegible]

[illegible] COVENT GARDEN, LONDON, W.C.

THE CARE OF CHILDREN IN SICKNESS AND HEALTH.

Councils on the Hygiene of Childhood.

By Father KNEIPP. 8vo, cloth. 5*s*.

In this little work Father Kneipp sets forth the happiness, responsibilities and duties of motherhood. He also gives simple directions for dealing with the usual diseases of children.

CHEMISTRY IN DAILY LIFE.

Twelve Popular Lectures by Dr. LASSAR-COHN, Professor of Chemistry in the University, Königsberg.

Translated into English by M. M. PATTISON MUIR, M.A., Fellow of Gonville and Caius College, Cambridge.

With 21 Illustrations. Crown 8vo, cloth. 6*s*.

"We have nothing but praise for the admirable series of lectures delivered by Prof. Lassar-Cohn. His scheme is too long to quote in detail, but it begins with the composition of air and the chemistry of breathing, and goes on to illumination, foods, agriculture, explosives, tanning, paper-making, soaps, glass, photography, metals and alloys. Nobody could fail to be interested by the homely method of setting forth difficult facts, and those in search of instruction will find it on every page."—*Pall Mall Gazette.*

THE ELEMENTS OF ELECTRO-CHEMISTRY TREATED EXPERIMENTALLY.

By Dr. ROBERT LÜPKE,

Headmaster of the Municipal Dorothea *Realgymnasium*, and Lecturer in the Imperial School of Posts and Telegraphs, Berlin.

With 54 figures in the text. Demy 8vo. 7*s*. 6*d*.

Translated from the Second Edition, Revised and Enlarged, by M. M. PATTISON MUIR, M.A.,

Fellow and Lecturer of Gonville and Caius College, Cambridge.

Electro-Chemistry is of much importance alike to the student of physics and the student of chemistry. The object of this book is to present, in condensed form, the results of the chief work, most of which has been done in the last twenty years, and much in the last ten years, in this department.

The book deals, firstly with the recent theories of electrolysis, secondly with van't Hoff's theory of solutions, and thirdly with the osmotic theory of the current from voltaic cells. The leading generalisations in each of these divisions of Electro-Chemistry are deduced from experiments of a simple character, which are fully described. This method of founding the scientific conclusion on the results of experiments which can be repeated in the lecture room and the laboratory with fairly simple apparatus, is the characteristic feature of the book. Attention is directed from time to time to the applications of Electro-Chemistry in arts and industries.

H. GREVEL & CO., 33, KING STREET, COVENT GARDEN, LONDON, W.C.

MURET'S
ENCYCLOPÆDIC DICTIONARY OF THE ENGLISH AND GERMAN LANGUAGES.

Edited by Professor Dr. ED. MURET and Dr. D. SANDERS.

Unabridged Edition.

Now ready. *English-German Dictionary*, 2 Vols. in 24 Parts, 4to, at 1*s.* 6*d.* each.

And *German-English Dictionary*. Part I. 4to. 1*s.* 6*d.*

MURET'S DICTIONARY is the Latest, the Largest, and by far the most Comprehensive of all English-German Dictionaries. It is the only one with the New German Orthography, and with the Pronunciation after the Phonetic System of Toussaint-Langenscheidt. It contains the Technical Terms in Art, Science, Commerce, and Manufactures; Anglo-Indian words, Provincialisms, and Americanisms; and is distinguished by its clear and concise arrangement, as well as by appropriate Examples. The German-English Part, edited by PROF. DR. D. SANDERS, has now begun.

DICTIONARY OF THE ENGLISH AND GERMAN LANGUAGES.

By Dr. FR. KOEHLER.

30th Edition, brought up to date, by Professor Dr. H. LAMBECK.

8vo, cloth, 7*s.* 6*d.*

"When a dictionary attains its thirtieth edition it may be laid down with a certain amount of confidence that the work is a success, and that those who require dictionaries (and who does not?) have found it to be a good book of reference. This book is useful to the German learning English as well as to the Englishman learning German. It is not, as so many dictionaries are, a one-sided production intended for use by the students of one nationality only. The present edition contains several new features and many additions."—*Publishers' Circular.*

PRACTICAL GRAMMAR OF THE GERMAN LANGUAGE.

With Reading Lessons, and a German-English and English-German Vocabulary.

By WILLIAM EYSENBACH.

New Edition. 8vo, cloth. 3*s.* 6*d.*

"It is decidedly '*practical.*' We like the gradual mode of presenting difficulty after difficulty, and the conversational tone of the exercises."—*Schoolmaster.*

H. GREVEL & CO., 33, KING STREET, COVENT GARDEN, LONDON, W.C.

JAN 9 - 1930